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NUTRIENT REMOVAL AND ADVANCED WASTE TREATMENT SYMPOSIUM HELD IN CINCINNATI, OHIO ON APRIL 29-30, 1969

Federal Water Pollution Control
Administration
Cincinnati, Ohio

April 1969

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TECHNICAL SYMPOSIUM

CLEAN WATER

NUTRIENT REMOVAL AND ADVANCED WASTE TREATMENT

CINCINNATI, OHIO
APRIL 29-30, 1969

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PRESENTATIONS

NUTRIENT REMOVAL AND ADVANCED WASTE TREATMENT SYMPOSIUM

APRIL 29-30, 1969

STOUFFER'S INN
CINCINNATI, OHIO

OHIO BASIN REGION
FEDERAL WATER POLLUTION CONTROL ADMINISTRATION
U.S. DEPARTMENT OF THE INTERIOR
CINCINNATI, OHIO

FOREWORD

This Symposium on Nutrient Removal and Advanced Waste Treatment was organized by the Ohio Basin Region of the Federal Water Pollution Control Administration to promulgate the latest developments in advanced waste treatment. The program was planned to focus attention on questions of what is known and what should be learned about nutrient removal and to assist workers in the field including consultants, industrialists, and water pollution control authorities.

A variety of methods have been used to remove part of the pollutants from wastewater before it is discharged. In many situations, existing methods are not adequate to provide the degree of treatment required to control pollution effectively. Research in waste treatment is being directed to development of methods ranging from lower-cost or higher-efficiency versions of conventional treatment technology to total wastewater purification systems capable of removing virtually all pollutants and even of producing reusable effluents. The Federal Water Pollution Control Administration's research in this area covers the entire field of waste treatment including treatment of industrial wastes, with special emphasis given to waste-treatment methods capable of total pollution control and purification of wastewater for deliberate reuse.

Richard A. Vanderhoof

Richard A. Vanderhoof

FIRST TECHNICAL SESSION

John Earl Richards, Moderator

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OBJECTIVES OF THE SYMPOSIUM

Francis M. Middleton

NUTRIENT REMOVAL

Phosphorus and nitrogen are fertilizing elements and are essential to life itself. Both elements occur in substantial amounts in municipal wastewaters. Conventional treatment methods were not designed to remove these nutrients, hence, removals that occur are haphazard and large unpredictable. Domestic wastewaters have been indicted as major sources of nutrients causing excessive growth of algae and the phosphorus and nitrogen content plays an important but not necessarily the only role in the fertilization process. However, the evidence of the role of phosphorus and nitrogen is sufficient that regulatory agencies are restricting the discharge of these elements.

It is the objective of the symposium to:

1. Provide an understanding of the variety of forms in which nitrogen and phosphorus occur in nature and wastewaters.
2. Describe briefly the techniques of measuring and expressing the results of measurement for phosphorus and nitrogen.
3. Discuss the up-to-date technology for removal of the nutrient elements. For phosphorus the following will be discussed:
    a. Removals by conventional treatment
    b. Removal by aluminum salts in conjunction with secondary treatment
    c. Removal by use of alum and lime after secondary treatment
    d. Removal by physical-chemical processes such as ion exchange, reverse osmosis and alumina columns

For nitrogen the following will be discussed:

a. Physical-chemical methods of removal

For both phosphorus and nitrogen a combined treatment system will be discussed.

4. The handling, reuse and disposal of chemical sludges resulting from treatment will be discussed as will the handling of conventional sludges.

ADVANCES IN TREATMENT

1. In addition to nutrient removal, the symposium will bring up-to-date advances in treatment to remove biochemical oxygen demand, solids, resistant organic residues, and mineral salts. Better use of plants we have, and modifications for more efficient treatment will be the subject of two talks. Filtration, microscreening and solids separation techniques will be a subject of discussion. Use of activated carbon to remove organic residues will be presented. Removal of inorganic salts by electrodialysis, ion exchange and reverse osmosis is a subject of the symposium.

2. The costs, design parameters, and capability of all the processes will be interwoven into the talks. Both an understanding of the processes and useful design information should result from the content of the talks and handouts. How to use the technology is a theme of the meeting.

3. The types and extent of research projects in pollution control being conducted in the Ohio Basin Region will be given.

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MEASUREMENT AND FORMS OF NITROGEN AND PHOSPHORUS

Edwin F. Barth

This topic is directed to nitrogen and phosphorus chemistry from a treatment standpoint.

I. Comparison of phosphorus and nitrogen

  A. Similarities

    1. Both non-metals

    2. Both have 3 and 5 as major chemical valance

    3. Both form similar types of compounds

  B. Differences

    1. Nitrogen is a stable gas

    2. Phosphorus is a reactive solid

    3. Most nitrogen compounds in wastewater are soluble

    4. Most phosphorus compounds form insoluble precipitates in wastewater

II. Interferences with phosphomolybdic assay of phosphorus

  A. Positive

    1. arsenic

    2. germanium

    3. selenium

  B. Negative

    1. Nitrite

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2. Hexavalent chromium

III. Biological cycle of elements

A. Carbon, nitrogen, sulfur and nitrogen

1. All can be converted to gaseous compounds

a) can be lost from system

B. Phosphorus

1. No oxidation or reduction to gaseous compounds

a) cannot be lost from system

2. Chemistry of phosphorus important to understanding eutrophication

IV. Importance of measuring total phosphorus

A. Phosphorus cycles between organic and inorganic forms

B. Insoluble phosphorus can be solubilized

C. Treatment efficiency must be based on total phosphorus assay

D. Wet ashing procedure recommended

E. Procedure in Standard Methods is for boiler water analysis

V. Forms of phosphorus

A. Procedural analysis can fractionate sample into 14 fractions

1. No need for treatment efficiency

2. May be useful in special investigations

B. Types and solubilities of phosphorus compounds

1. Requires total phosphorus assay

VI. Phosphomolybdic assay

A. An empirical operational procedure

1. Variables must be controlled

a) acid concentration

b) time

c) reductant

d) temperature

B. Present technique cannot differentiate forms such as ortho, poly, organic, or mineral phosphorus

C. Referee phosphorus procedure needed

VII. Nitrogen series determinations were classic sanitary analyses
    A. BOD substituted as measure of efficiency
    B. Nitrification now considered important

VIII. Forms of nitrogen in wastewater
    A. Analytical procedures specific for each form
    B. Quantitation requires complete series
    C. Biological transformations of nitrogen

IX. Preservation of samples for nitrogen analyses
    A. Van Slyke reaction
    B. Freezing

X. Methemoglobinemia
    A. Nitrite and nitrate should both be determined

XI. Automated methods
    A. Great need for more extensive analyses
        1. Must be careful data is accurate

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TABLE I

Determination of Various Phosphorus Forms

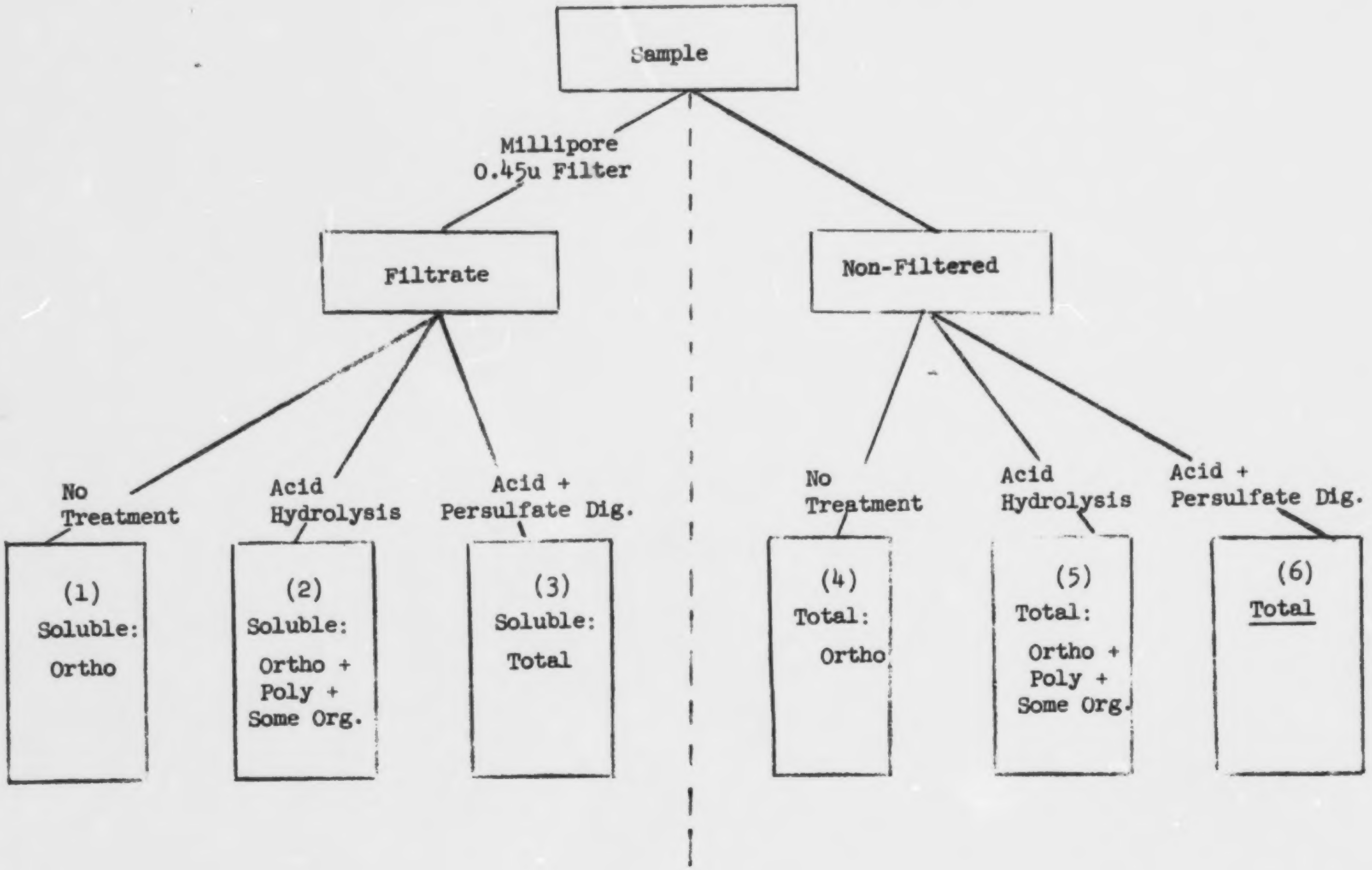

Sample
Millipore 0.45u Filter
Filtrate
Non-Filtered
No Treatment
Acid Hydrolysis
Acid + Persulfate Dig.
(1) Soluble: Ortho
(2) Soluble: Ortho + Poly + Some Org.
(3) Soluble: Total
No Treatment
Acid Hydrolysis
Acid + Persulfate Dig.
(4) Total: Ortho
(5) Total: Ortho + Poly + Some Org.
(6) Total

TABLE II

Data Treatment	Phosphorus Components Determined
	A. Soluble Forms
1	1) ortho
2	2) ortho + poly + some org's.
3	3) total
2 - 1	4) poly + some org's.
3 - 2	5) most org's.
	B. Total Forms
4	6) ortho
5	7) ortho + poly + some org's.
6	8) total
5 - 4	9) poly + some org's.
6 - 5	10) most org's.
	C. Particulate Forms
4 - 1	11) ortho
(5-4) - (2-1)	12) poly + some org's.
(6-5) - (3-2)	13) most org's.
6 - 3	14) total

TABLE III

Forms and Measurements of Phosphorus

Phosphoric Anhydride	P_4O_{10} (usually calculated as P_2O_5)

Orthophosphates Found in Water

Phosphoric acid	H_3PO_4 below pH 2.2
Dihydrogen phosphate ion (monovalent)	$H_2PO_4^-$ from pH 2.2 to 7.2
Monohydrogen phosphate ion (divalent)	$HPO_4^{=}$ from pH 7.2 to 12.4
Phosphate ion (trivalent)	$PO_4^{\equiv}$ above pH 12.4
Dicalcium phosphate	$CaHPO_4$ from pH 6 to 8

(Tricalcium phosphate, $Ca_3(PO_4)_2$, does not form in water)

Hydroxyapatite	$Ca_5OH(PO_4)_3$ above pH 7-8
Fluorapatite	$Ca_5F(PO_4)_3$ above pH 7

Aluminum hydroxide adsorbs $HPO_4^{=}$ from pH 5 to 10

Aluminate ion $Al(OH)_4^-$ forms above pH 10

Ferric hydroxide adsorbs $HPO_4^{=}$ above pH 4

Magnesium hydroxide flocculates colloidal phosphates above pH 10-11

Polyphosphates

All polyphosphates hydrolyze slowly to orthophosphates

Sodium Trimetaphosphate	$Na_3(PO_3)_3$ -- a ring compound
Sodium Polymetaphosphate	$(NaPO_3)_n$ -- a long chain

(there is no justification for the name "hexametaphosphate")

Sodium Pyrophosphate	$Na_4P_2O_7$
Sodium Tri Polyphosphate	$Na_5P_3O_{10}$

Organic Phosphates

Esters and anhydrides	$ROPO_3^{=}$, $ROPO_3PO_3^{=}$
Phosphagens	$RNPO_3^{=}$

Reference

(1) Van Wazer, J. R. Phosphorus and Its Compounds. Interscience 1958.

TABLE IV

PHOSPHORUS COMPOUNDS CLASSIFIED BY CHEMICAL AND SOLUBILITY RELATIONS(1)

Form	Water Soluble(2)	Insoluble(2)
1. Ortho phosphates $(PO_4)^{-3}$	Combined with monovalent cations such as H, Na, K, NH_4	Combined with multi valent cations such as $CA^{+2}Al^{+3}Fe^{+3}$
2. Poly phosphates $(P_2O_7),^{-4}(P_3O_{10})^{-5}(P_3O_9)^{-3}$ and others depending upon the degree of dehydration.	(a) as in 1 (above), but solubility decreases as molecular weight increases	(a) as in 1 (above) (b) multi P polyphosphates (high mol. wt.) including the "glassy" phosphates
3. Organic phosphorus R-P, R-P-R (3) (unusually varied nature)	(a) certain chemicals (b) degradation products (c) enzyme P (d) phosphorylated nutrients	(a) certain chemicals (b) cell mass, may be colloidal or agglomerated (c) soluble P sorbed by insoluble residues
4. Mineral phosphorus	(a) as in 1 (above), but solubility decreases for complex forms	(a) as in 1 (above) (b) geological P such as phosphosilicates (c) certain mineral complexes

(1) Table drawn from a lecture, "Determination of Phosphorus in the Aqueous Environment," by F. Ludzack, FWPCA Training Activities, Ohio Basin Region.

(2) Used to indicate usual state under common conditions.

(3) R represents an organic radical, P represents P, PO_4, or its derivatives.

TABLE V

Effect of Varing Sulfuric Acid - Ammonium Molybdate Ratio on Heteropoly Blue Color Development
(Stannous chloride in glycerine reductant)

Acid Molybdate Reagent Composition		Normality* of acid in final 100 ml assay volume	Absorbancy (O.D.)	
Ammonium Molybdate gm/100 ml	Concentrated Sulfuric Acid ml/100 ml		Distilled Water	0.05 mg P Standard
2.0	5	0.072	> 2.0	> 2.0
2.0	10	0.144	0.805	1.00
2.0	15	0.216	0.260	0.580
2.0	20	0.288	0.036	0.475
2.0	25	0.360	0.004	0.415
2.0	30	0.432	0.000	0.365
2.0	35	0.504	0.000	0.345
2.0	40	0.576	0.000	0.252
2.0	50	0.720	0.000	0.060
2.0	60	0.864	0.000	0.012

*Calculated normality of H_2SO_4 in the 100 ml final volume produced by using 4.0 ml of the particular acid molybdate solution.

TABLE VI

Nitrogen Forms in 1:1 Mixture of High-Rate and Nitrified Effluents

Nitrogen Form	High-Rate Effluent	Nitrified Effluent	Denitrified Effluent	Oxidized Nitrogen Removal	Over-All Removal
Organic-N	5	2	3		
Ammonia-N	10	0	5		
NO_2-N	-	1 > 13	0.5 > 1.0		
NO_3-N	-	12	0.5	92%	
Sum	15	15	9		40%

Element	Symbol	Valences	Usual form
Nitrogen	N	3, 5, 1, 2, 4	Gas
Phosphorus	P	3, 5, 1, 4	Waxy solid
Arsenic	As	3, 5	Metallic solid

Compounds with similar properties

HNO_3	N_2O_3	NCl_3	NH_3
H_3PO_4	P_2O_3	PCl_3	PH_3
H_3AsO_4	As_2O_3	$AsCl_3$	AsH_3
↑ Acid strength	↑ Reactivity	↑ Unstable nature	↑ Stable nature

Similar compounds with different properties

Soluble: $Ca(NO_3)_2$ $Al(NO_3)_3$ $Fe(NO_3)_3$

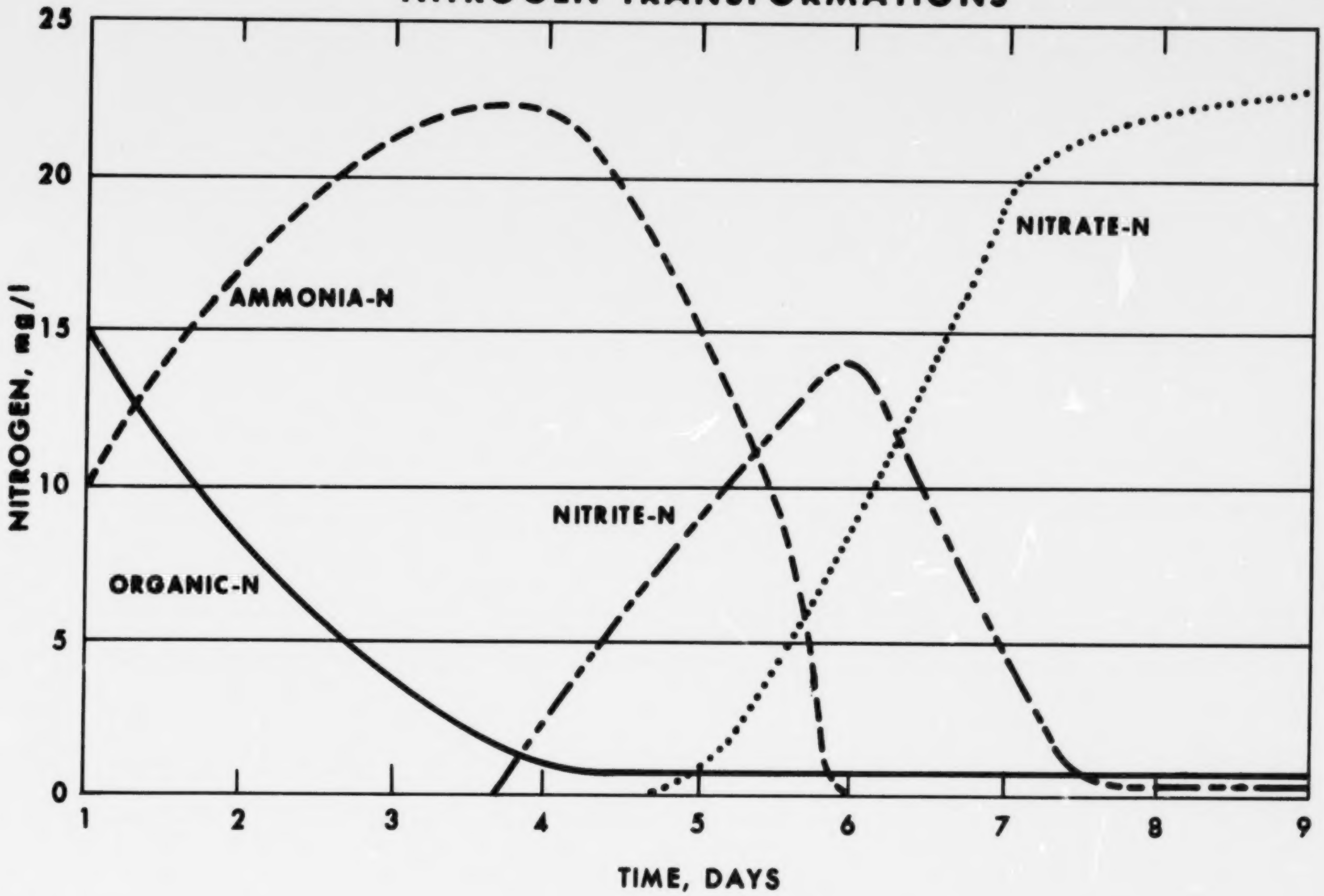
Insoluble: $Ca_3(PO_4)_2$ $AlPO_4$ $FePO_4$ $(NH_4)MgPO_4$

ELEMENTS AND BIOLOGICAL TREATMENT

ELEMENT	BIOLOGICAL REACTION	RESULT OF TREATMENT NET LOSS
OXYGEN	OXIDATION AND/OR REDUCTION	CO_2 CH_4
CARBON		
HYDROGEN		H_2 H_2O
NITROGEN		N_2
SULFUR		H_2S

		NO LOSS
PHOSPHORUS	NO OXIDATION NO REDUCTION	ORGANIC PHOSPHORUS ⇅ INORGANIC PHOSPHORUS

NITROGEN TRANSFORMATIONS



VAN SLYKE REACTION

$$RNH_2 + NO_2^- \xrightarrow{\text{acid}} ROH + N_2\uparrow + H_2O$$

PHOSPHORUS REMOVAL BY CONVENTIONAL TREATMENT

Robert L. Bunch

I. WASTE TREATMENT FACILITIES

A. Population receiving treatment

Only 63% of the population in the United States is connected to some type of sewer. Of the population that is served, only 88% receive some type of treatment.

B. Type of treatment facilities

1. Classification by population

   In 1962 only 30% of the population's wastes received secondary treatment.

2. Classification by processes

   Activated sludge treatment plants amount to only 12% of all secondary treatment facilities. The trickling filter method of waste treatment far exceeds all other methods of treatment.

II. PHOSPHATES IN WASTEWATER

The phosphate content of wastewater treatment plant effluents has increased appreciably in the last ten years. The quantity now appears to have reached a plateau.

A. Trends in phosphate production

B. Contribution by human excretion and detergent builders.

C. Contribution by fertilization and runoff.

III. FACTORS AFFECTING PHOSPHORUS REMOVAL

A. Nutrient imbalance of sewage

Most sewages have an excess of nitrogen and phosphorus relative to the amount of carbon required for bacteria growth.

B. Digester recycle

The actual amount of phosphorus removed depends on the amount of sludge wasted. If digester supernatant is returned to the plant, the only phosphorus removed will be that associated with the digested sludge.

C. Mineral content of the wastewater

D. Plant operations

The literature indicates that several factors exert an influence on phosphorus removal. The most commonly considered variables are:

1. Aeration time and rate of air supply

   Aeration rates in the order of 3 to 7 cfm/gal and detention times of 4 to 6 hours appear to be desirable.

2. Concentration of mixed liquor suspended solids

   For maximum BOD reduction it is necessary to carry at least 2 lb of solids under aeration per pound of daily 5-day BOD input.

3. Concentration of dissolved oxygen in aerator

   Where increased phosphorus removals have been experienced, they did not occur until 1.5 to 2.0 mg/l DO levels were obtained.

4. Time of sludge retention in clarifier

   Solids detention time in final clarifier should be as short as possible.

IV. PHOSPHORUS REMOVAL BY TREATMENT PLANTS

Conventional treatment plants show a wide range of efficiencies for phosphorus removal. These range from 5 percent for primary plants to 30-50 percent for activated sludge plants. There are some plants that are removing much more; for example, the San Antonio Rilling Plant and the treatment plant at Baltimore, Maryland.

PHOSPHORUS REMOVAL BY MINERAL ADDITION

Richard C. Brenner

I. CURRENT APPROACHES TO REMOVING MAJOR FRACTION OF PHOSPHORUS FROM WASTEWATER

  A. Increase biological uptake

    1. Eliminate digester supernatant recycle

    2. Enhance cell synthesis

      a. Increase carbon loading to biological process by eliminating primary settler

    3. Control conventional operating parameters

    4. Controlled tertiary algae production and harvesting

  B. Chemical precipitation

    1. Separate tertiary processes using biological effluent as feed

      a. Lime - Tahoe

      b. Alum - Nassau County, N. Y.

    2. Removal in primary settler

      a. Iron plus polymer - Dow

      b. Lime plus recalcining - Dorr-Oliver

  C. Combined chemical-biological interaction (Mineral Addition)

    1. Direct addition of metallic salts to activated sludge aerator

      a. Iron salts

      b. Aluminum salts

    2. Alternative application points

      a. Primary effluent

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b. Mixed liquor exit to clarifier

c. Sludge recycle

d. Prior to biological flocculation

3. Net result

a. Precipitation of phosphorus directly in aerator

b. Formation of biological-chemical sludge

c. Continuous recycle of metallic-rich sludge

d. Enhanced adsorption and flocculation of chemical precipitate

e. Removal of precipitated phosphorus in waste sludge

II. FORMS OF MINERAL ADDITION

A. European practice

1. Use of iron compounds - principal proponent, Dr. Thomas from Switzerland

B. U.S.A. practice

1. Major research and development efforts to date centered on aluminum compounds - primary developers, Barth and Ettinger

a. Aluminum sulfate (Alum) - Nesbitt, Penn State

b. Sodium aluminate

C. Comparison of iron and aluminum

1. Iron forms colored compounds

2. Iron undergoes oxidation-reduction reactions

3. All forms of iron compounds strongly acidic

4. Aluminum available in acidic and basic forms

a. Allows choice to fit wastewater characteristics

    5. Iron compounds more available as impure or waste streams
        a. Not necessary to have high grade compound
        b. Cheaper as waste stream

III. ADVANTAGES OF MINERAL ADDITION USING ALUMINUM COMPOUNDS

- A. Low capital expenditure
    - 1. Dual use of aerator
        - a. Mixing by diffusion apparatus
        - b. Residence provided for reactions
    - 2. Makes use of existing final settler
    - 3. Requires dosing equipment and storage tanks only
- B. Large surface area of floc readily available
    - 1. Biological-chemical interaction
        - a. Adsorption to floc surface
        - b. Coagulation of fine precipitate particles
    - 2. Reduces chemical requirement compared to strict tertiary unit process
- C. Enhances mixed liquor settling characteristics
    - 1. Improved SDI
- D. Reduces effective organic loading
    - 1. Higher mixed liquor solids
- E. Reduces supernatant phosphorus recycle
    - 1. Phosphorus not released from aluminum precipitate during anaerobic digestion
    - 2. Phosphorus removed from plant in digested sludge

IV. COMPARISON OF ALUM AND ALUMINATE

A. Chemical comparison

  1. Alum acidic

    a. Uses up alkalinity reserve

    b. Causes pH to decrease

    c. Aluminum ion is cation

  2. Aluminate basic

    a. Natural buffer

    b. pH elevates slightly

    c. Aluminum ion part of anion radical

  3. Alum compounds contain more water

  4. Aluminate compounds contain higher percentage of Al^{+++}

B. Pilot scale comparison (200 gpd)

  1. Identical feed - parallel study

  2. Moderate alkalinity

  3. Better removal of all major contaminants with aluminate

    a. Improved COD and suspended solids removal significant

    b. Removal of phosphorus dependent on chemical dose

  4. Alkalinity reduced by alum

    a. Alkalinity near zero at times

    b. Resultant lowering of pH

    c. Marked increase in turbidity

    d. Effluent phosphorus breakthrough at times of organism aggravation

      (1) Indicative of poorer solids capture

      (2) Fine particle carry-over

C. Overall phosphorus removal - pilot scale study

1. Function of Al/P ratio

   a. Better unit utilization of Al at lower doses

   b. Better overall phosphorus removal at higher doses

2. Alum and aluminate exhibit equal capability for total phosphorus removal

   a. Solubility of aluminum phosphate decreases as pH approaches 6

   b. Poorer fine floc capture as pH approaches 6

   c. Offsetting characteristics

3. Effect of Al dose on total phosphorus removal

   a. 80% removal at 1/1 dose (by wt) of Al/P

   b. 90% removal at 1.2/1 dose (by wt) of Al/P

   c. Diminishing return above 1.2/1

   d. Maximum removal at ratio of 1.4/1 to 1.5/1

   e. Removal decreases if dose pushed higher

      (1) Greater resistance to settling of aluminum phosphate particles

      (2) Filtered sample would still show high removal

D. Large scale comparison (2 mgd)

1. Comparison on sequential basis - Pomona, California

2. Wastewater - high alkalinity

3. Filtered phosphorus removal about equal

4. Better removal with alum on unfiltered samples

   a. Sufficient alkalinity to prevent upset with alum

   b. Basic characteristic of aluminate less suitable with this wastewater

E. Side effects

  1. Alum introduces sulfate ions

  2. Aluminate introduces sodium ions

  3. Increase in total dissolved solids about 6 times greater with alum

F. Interpretation of studies

  1. Choice of compound depends on wastewater characteristics

    a. Aluminate better suited to low to moderately alkaline wastewaters

    b. Alum better suited to highly alkaline wastewaters

  2. Must be cognizant of extraneous pollution introduced by aluminum compounds

V. OTHER LARGE SCALE DEMONSTRATIONS

A. Completed studies

  1. Xenia, Ohio (1 mgd)

    a. Activated sludge

    b. Six-week field study using aluminate

    c. Phosphorus removal approached 90% at ratios of 1.5/1 to 1.8/1 (by wt) of Al/P

    d. Improved sludge settling and concentration

  2. Fairborn, Ohio (3 mgd)

    a. Trickling filter plant

    b. Four-week field study dosing aluminate to 1/3 of plant

    c. Aluminate fed just ahead of distribution over rock media

    d. Overall phosphorus removal across dosed filter - about 65%

e. Overall phosphorus removal across control filter - about 15%

f. Less efficient that activated sludge

(1) Insufficient mixing

(2) Reduced residence time

(3) Absence of freely moving biological flocculator mechanism

g. No adverse effects on filter operation or performance

B. Future and in-progress grant and contract work

1. Penn State University - 2 mgd

2. University of Texas - 0.75 mgd

3. University of Notre Dame - 50,000 gpd

4. Manassas, Virginia - 1 mgd

5. New York State Department of Health - 0.1 mgd

6. Detroit, Michigan - 7,000 gpd

VI. COST CONSIDERATIONS FOR MINERAL ADDITION

A. Existing pricing structure

1. Alum cheaper

a. Greater existing market

b. Commodity shipping rates

2. Aluminate price trend is downward for bulk purchases

3. Alum price structure is stable

4. Both compounds available in liquid and dry forms

B. Chemical cost of removing phosphorus with aluminum

1. Directly proportional to phosphorus concentration

2. Unit cost same regardless of plant size

3. Cost using alum affected by need for buffering

4. At this point in time

    a. Alum cheapest

    b. Alum plus lime next in line

    c. Aluminate most expensive

5. Costs vary from 2-1/2 to 4-1/2 cents per thousand gallons treated

    a. Depends on chemical used

    b. Depends on phosphorus concentration

    c. Depends on degree of removal desired

C. Capital costs

    1. Relatively modest investment

        a. Maximum $40,000 to $100,000 depending on plant size

    2. Requirements are storage tanks and dosing system

    3. Dosing system

        a. Continuous flow and phosphorus monitoring needed to properly match chemical dose to influent phosphorus

        b. Measurements used to automatically adjust pump speed and stroke travel distance

        c. Elements comprise dual open loop controlled dosing system

D. Total cost of removing phosphorus

    1. Major cost associated with chemicals

    2. Increment varies from 1/4 to 1/2 of cost for carbon and solids removal depending on plant size

        a. Percent increment smallest for small plants

        b. Percent increment greatest for large plants

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The following slides will be used. Reproductions of the slides are attached in the order presented.

Slide No.	Title
1	Approaches to Phosphorus Removal
2	Phosphorus Control Basic Systems
3	Combined Chemical-Biological, Variations of Basic Systems
4	Advantages of Combined Biological and Chemical Processes
5	Comparison of Phosphorus Removal by Mineral Addition and Tertiary Treatment Using Alum (Pomona, L.A.C.S.D.)
6	Effect of Aluminum on Sludges and Supernatant
7	Characteristics of Aluminum Salts
8	Effect of Aluminum Salts on pH
9	Comparison of Alum Dosed and Aluminate Dosed Activated Sludge Units
10	Effect of Mineral Addition on Alkalinity of Systems
11	Effect of Mineral Addition on pH of Systems
12	Comparison of Effluent Turbidity
13	Comparison of Effluent Phosphorus
14	Aluminum Utilization versus Aluminum Dose
15	Phosphorus Removal versus Aluminum Dose
16	Pomona Date, Average Values
17	Photograph of Pomona Mixed Liquor (Reproduction not available for outline)
18	Side Effects of Aluminum Addition
19	Example of Side Effects from Pilot Plant Study
20	Little Miami Treatment Plant - Average Phosphorus Values for 5-Day Periods

21 Fairborn, Ohio Trickling Filter Plant, Schematic Diagram
22 Fairborn, Ohio Trickling Filter (Percent Removals)
23 Bulk Delivered Chemical Price Structure for Projecting Phosphorus Removal Costs
24 Chemical Cost for 90% Phosphorus Removal
25 Chemical Costs of Removing Phosphorus by Mineral Addition
26 Dual Automatic Open Loop Chemical Feed System for Controlled Dosing
27 Total Treatment Costs - Activated Sludge Treatment Plus Phosphorus Removal

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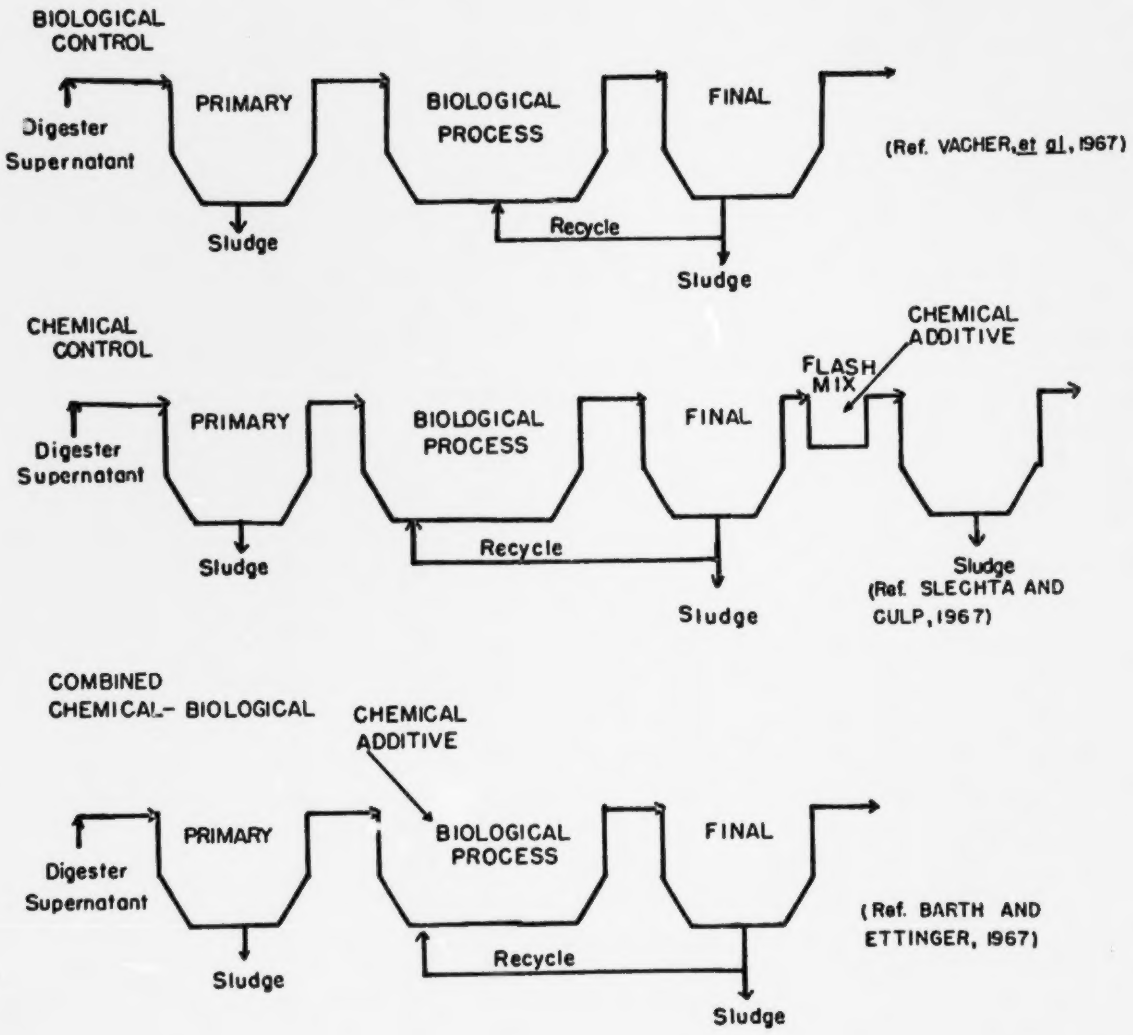
APPROACHES TO PHOSPHORUS REMOVAL

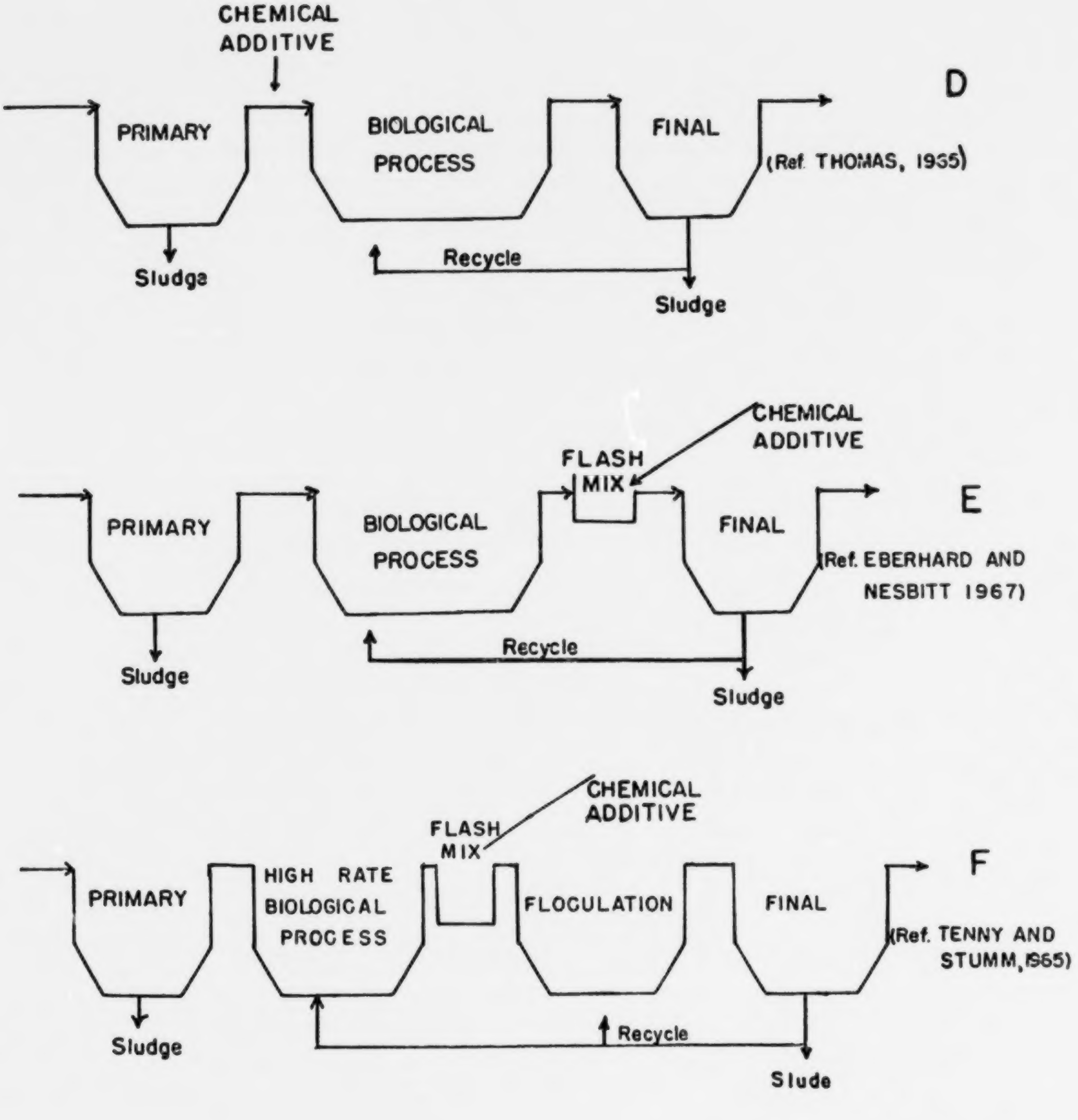
CONTROL OF BIOLOGICAL UPTAKE

CHEMICAL TREATMENT OF BIOLOGICAL EFFLUENT OR PROCESS STREAM TO FORM SLIGHTLY SOLUBLE PHOSPHORUS COMPOUNDS

COMBINATION OF THESE TWO ABOVE APPROACHES


BIOLOGICAL CONTROL
Digester Supernatant
PRIMARY
Sludge
BIOLOGICAL PROCESS
Recycle
FINAL
Sludge
(Ref. VACHER, et al, 1967)
CHEMICAL CONTROL
Digester Supernatant
PRIMARY
Sludge
BIOLOGICAL PROCESS
Recycle
FINAL
Sludge
FLASH MIX
CHEMICAL ADDITIVE
Sludge
(Ref. SLECHTA AND CULP, 1967)
COMBINED CHEMICAL- BIOLOGICAL
CHEMICAL ADDITIVE
Digester Supernatant
PRIMARY
Sludge
BIOLOGICAL PROCESS
Recycle
FINAL
Sludge
(Ref. BARTH AND ETTINGER, 1967)

PHOSPHORUS CONTROL BASIC SYSTEMS

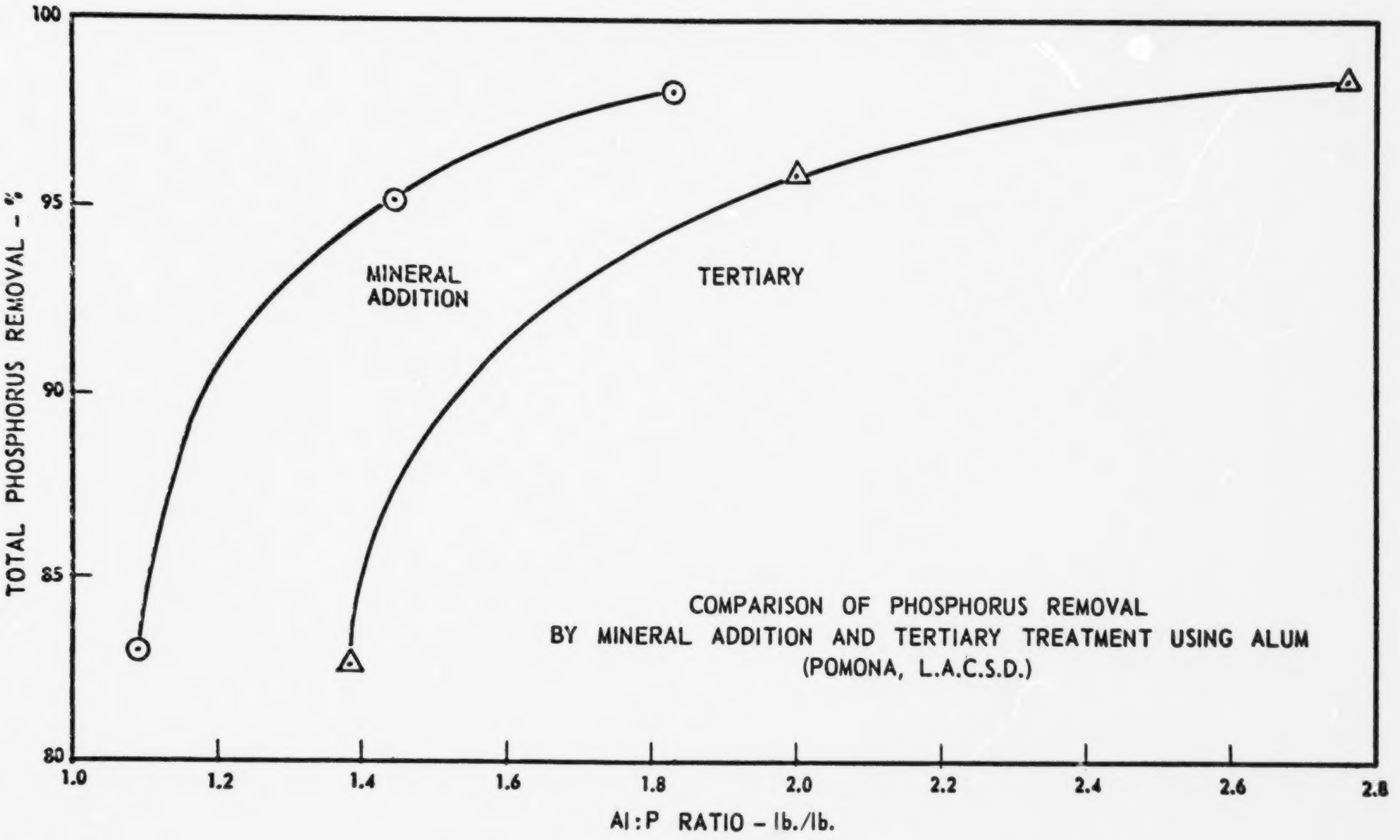

CHEMICAL ADDITIVE
PRIMARY
BIOLOGICAL PROCESS
FINAL
D
(Ref. THOMAS, 1955)
Sludge
Recycle
Sludge
CHEMICAL ADDITIVE
FLASH MIX
PRIMARY
BIOLOGICAL PROCESS
FINAL
E
(Ref. EBERHARD AND NESBITT 1967)
Sludge
Recycle
Sludge
CHEMICAL ADDITIVE
FLASH MIX
PRIMARY
HIGH RATE BIOLOGICAL PROCESS
FLOCULATION
FINAL
F
(Ref. TENNY AND STUMM, 1965)
Sludge
Recycle
Slude

COMBINED CHEMICAL- BIOLOGICAL, VARIATIONS OF BASIC SYSTEMS

ADVANTAGES OF COMBINED BIOLOGICAL AND CHEMICAL PROCESSES

Add Mineral Supplement Directly to Aerator

1. Dual Use of Aerator
   a) Mixing by Diffusion Apparatus
   b) Residence Time for Reactions
2. Uses Existing Final Settler
3. Large Surface Area of Floc Available
   a) Biological - Chemical Interaction
   b) Reduces Chemical Requirement
4. Improves Mixed Liquor Settling
5. Reduces Effective Organic Loading
6. Reduces Supernatant Phosphorus Recycle
   a) Phosphorus not Released during Digestion
   b) Phosphorus Removed from Plant in Digested Sludge



COMPARISON OF PHOSPHORUS REMOVAL
BY MINERAL ADDITION AND TERTIARY TREATMENT USING ALUM
(POMONA, L.A.C.S.D.)

EFFECT OF ALUMINUM ON SLUDGES AND SUPERNATANT

1. HIGH-RATE MIXED LIQUOR CHARACTERISTICS

	MLSS mg/l	MLVSS mg/l	% VOLATILE	SDI	ORGANIC LOAD lb COD/day/ lb MLVSS
BEFORE Al^{+++}	1,450	900	62	0.44	2.6
AFTER Al^{+++}	3,385	1,740	51	1.12	1.6

2. PERCENT PHOSPHORUS IN SLUDGES - TOTAL SOLIDS BASIS

	PRIMARY	WASTE ACTIVATED	MIXED PRIMARY PLUS W. ACTIVATED	DIGESTED
BEFORE Al^{+++}	1.1	2.1	1.6	2.2
AFTER Al^{+++}	1.1	6.2	4.5	5.2

3. TOTAL PHOSPHORUS IN SUPERNATANT - mg/l

BEFORE Al^{+++}	170
AFTER Al^{+++}	60

CHARACTERISTICS OF ALUMINUM SALTS

	(ALUM) ALUMINUM SULFATE		SODIUM ALUMINATE	
CHEMICAL FORMULA	$Al_2(SO_4)_3$		$Na_2Al_2O_4$ ($NaAl(OH)_4$ DISSOLVED)	
pH of 1% SOLUTION OF DRY CHEMICAL	3.5		11.9	
	DRY FORM	LIQUID FORM	DRY FORM	LIQUID FORM
% STATED CHEMICAL WT. BASIS	57	28	74	46
% Al - WT. BASIS	9.0	4.4	24.4	15.1

EFFECT OF ALUMINUM SALTS ON pH

---

1. ADDITION OF ALUMINUM SULFATE TO WATER

$$Al(SO_4)_3 + 6\ H_2O \rightleftharpoons 2\ Al(OH)_3 + 3\ H_2SO_4$$

$$2\ Al^{+++} + 6\ H_2O \rightleftharpoons 2\ Al(OH)_3 + 6\ H^+$$

pH DECREASES

2. ADDITION OF SODIUM ALUMINATE TO WATER

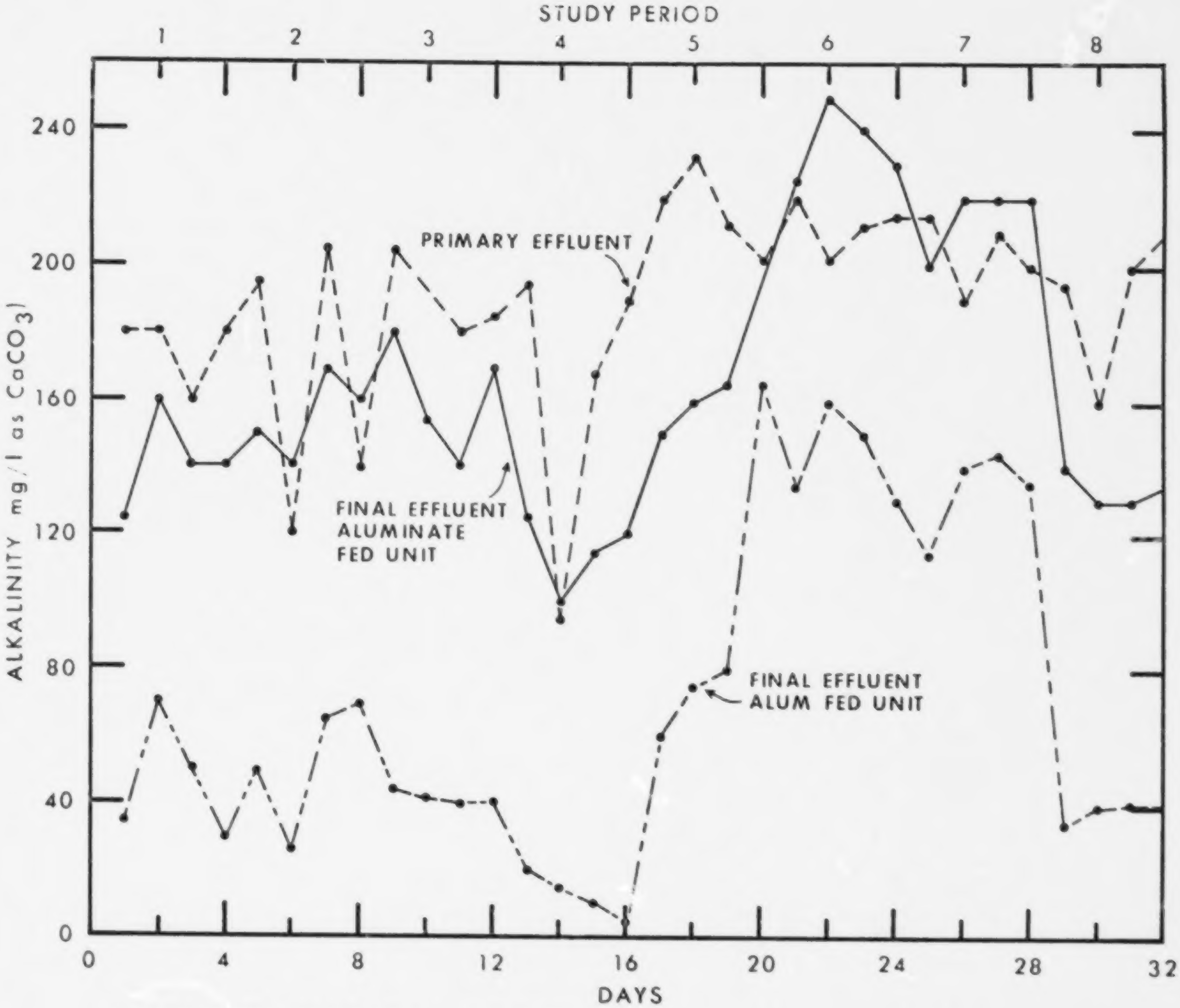
$$NaAl(OH)_4 \rightleftharpoons Al(OH)_3 + NaOH$$

$$\left[Al(OH)_4\right]^- \rightleftharpoons Al(OH)_3 + OH^-$$

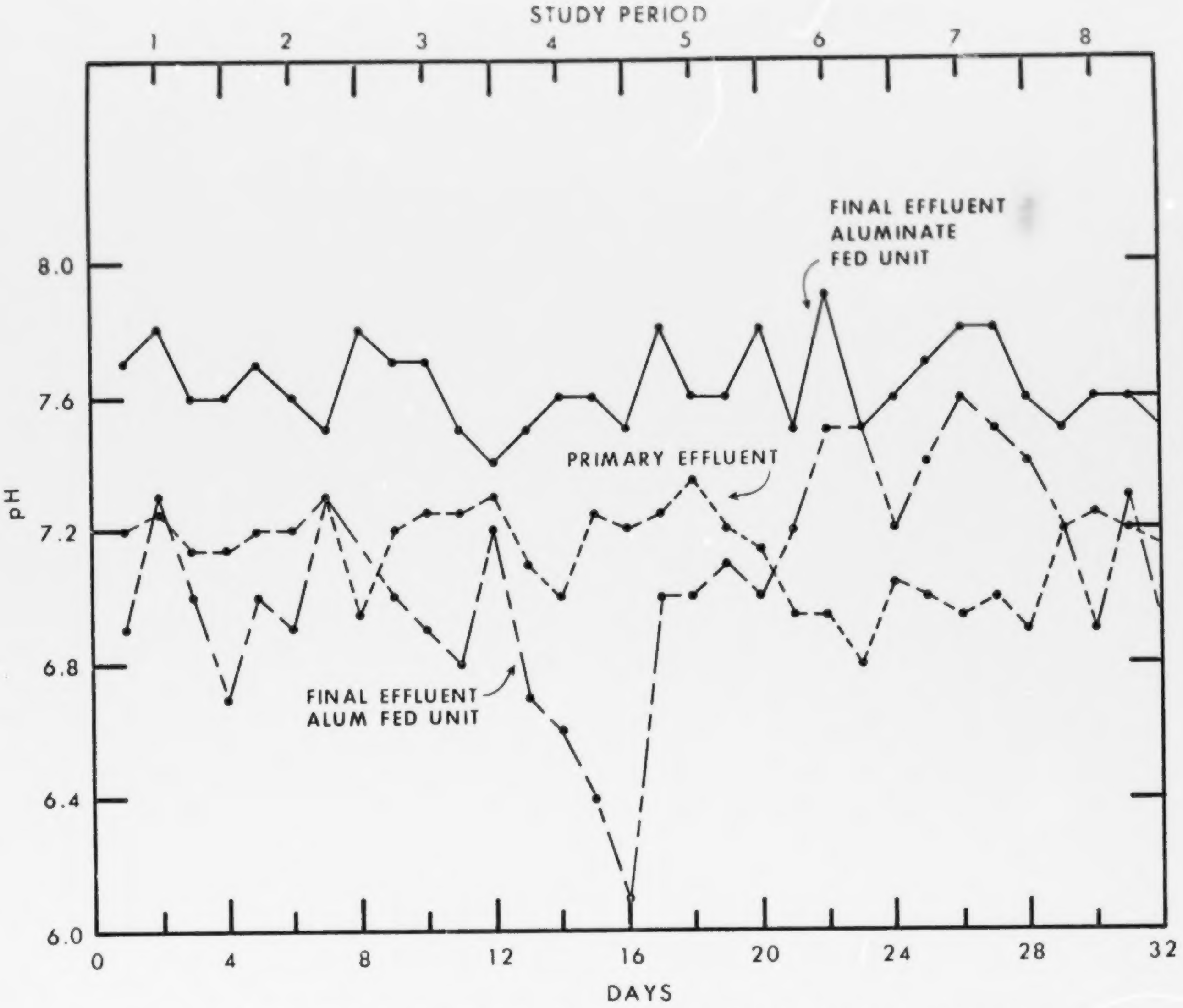
pH INCREASES

COMPARISON OF ALUM DOSED AND ALUMINATE DOSED ACTIVATED SLUDGE UNITS

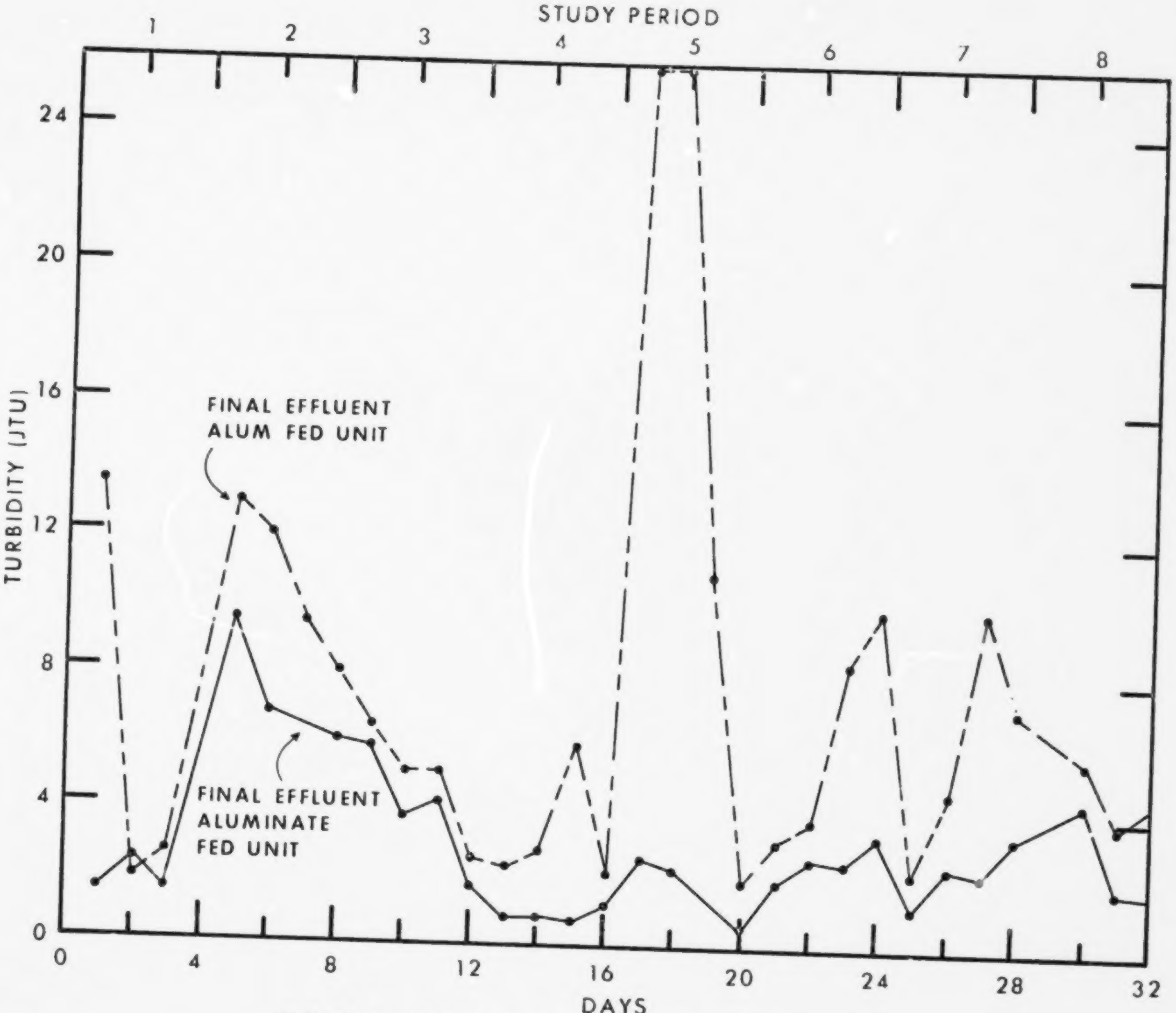
CONSTITUENT	RAW SEWAGE mg/l	FINAL EFF - ALUMINATE DOSED UNIT		FINAL EFF - ALUM DOSED UNIT	
		mg/l	% REMOVAL	mg/l	% REMOVAL
COD	310	23	93	35	89
TOTAL PHOS.	11.6	1.2	90	2.0	83
NITROGEN (ALL FORMS)	23.0	9.4	59	10.7	53
SUSPENDED SOLIDS	157	7	96	21	87
TURBIDITY - PRI EFF - (JTU)	46	3.1	93	7.4	85
ALKALINITY (as $CaCO_3$)	182	165		67	
pH	7.2	7.6		6.9	



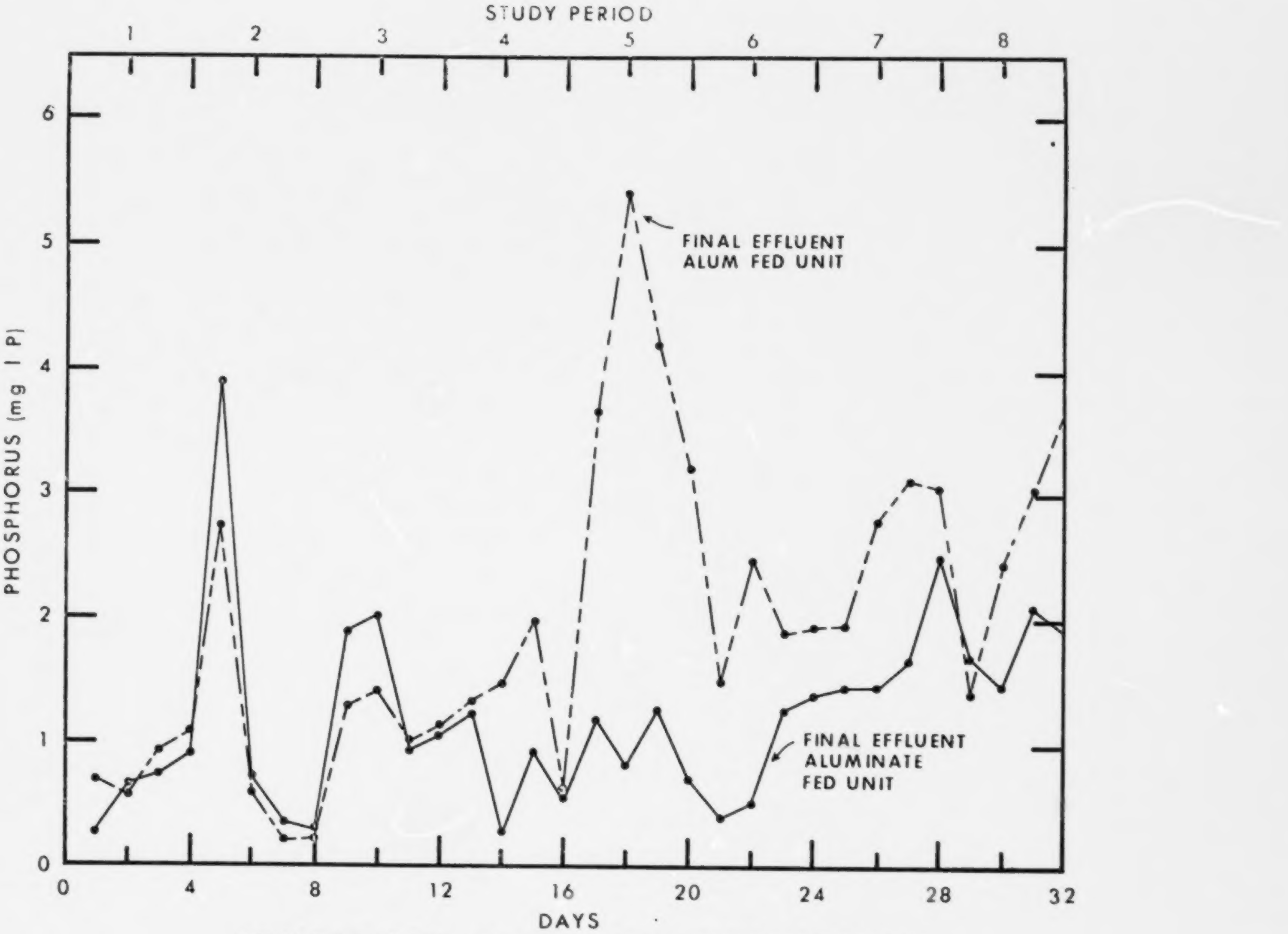
EFFECT OF MINERAL ADDITION ON ALKALINITY OF SYSTEMS



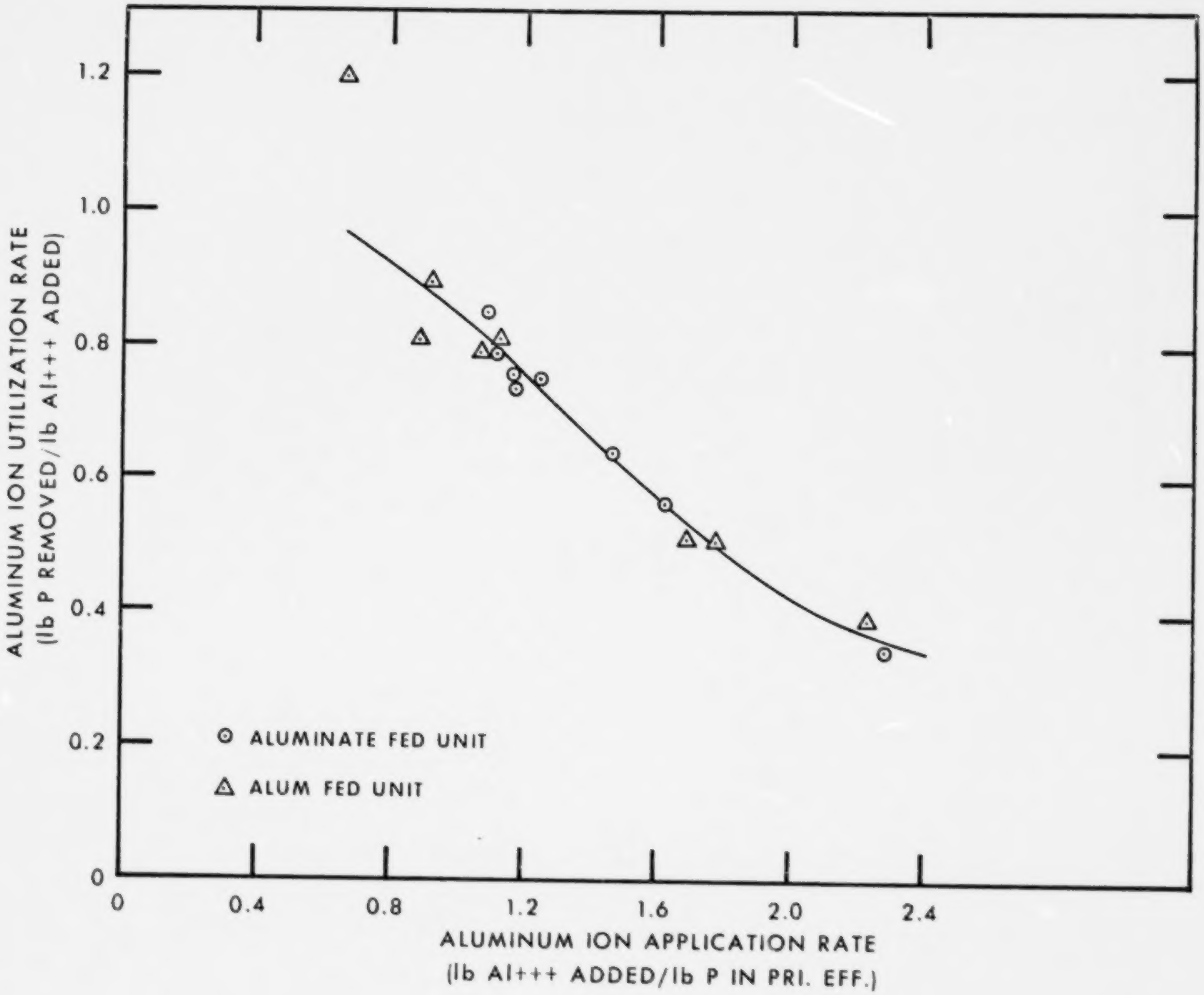
EFFECT OF MINERAL ADDITION ON pH OF SYSTEMS

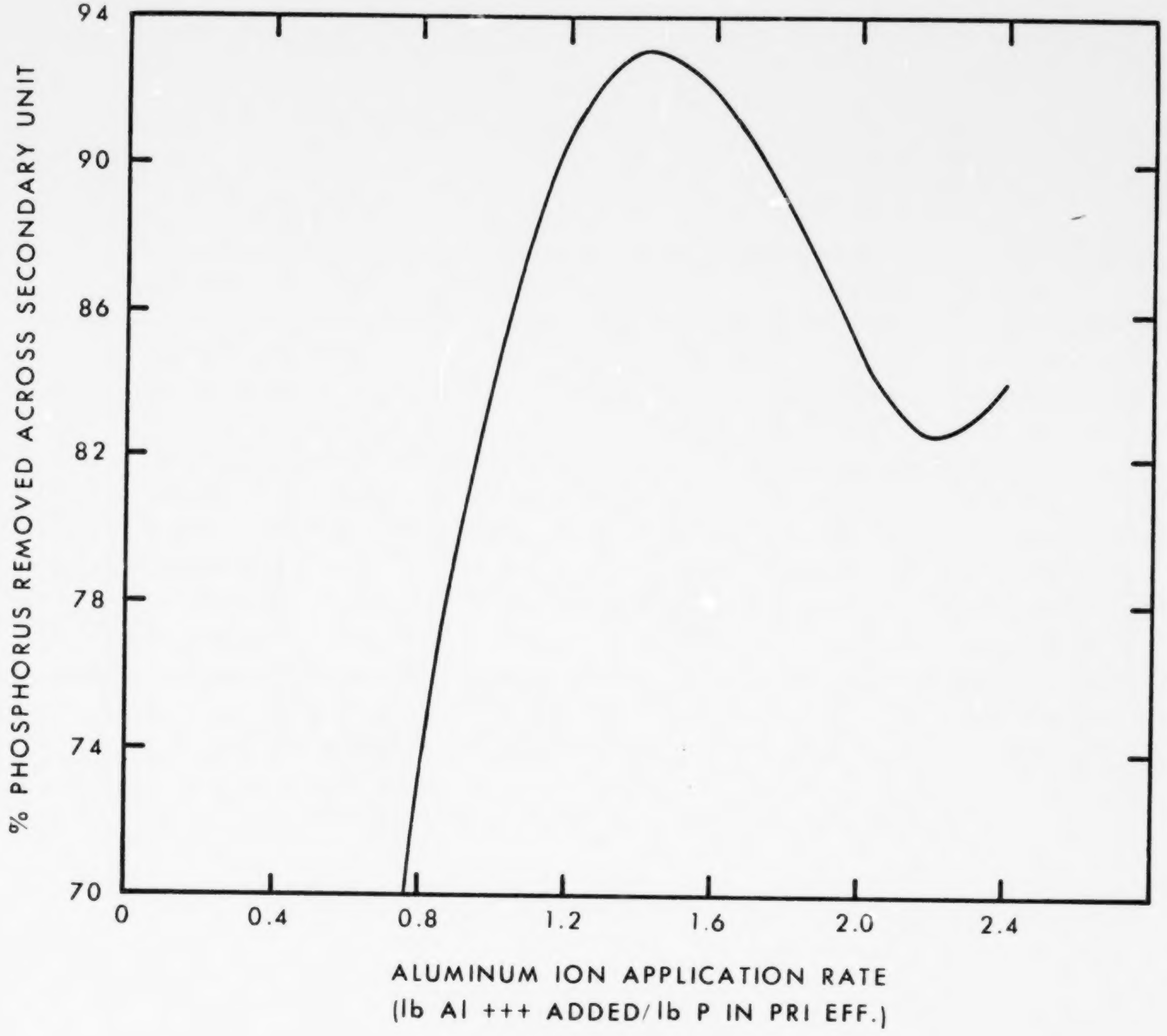


COMPARISON OF EFFLUENT TURBIDITY



COMPARISON OF EFFLUENT PHOSPHORUS*
(* TOTAL PHOSPHORUS ASSAY)


ALUMINUM ION UTILIZATION RATE
(lb P REMOVED/lb Al+++ ADDED)
1.2
1.0
0.8
0.6
0.4
0.2
0
0.4
0.8
1.2
1.6
2.0
2.4
ALUMINUM ION APPLICATION RATE
(lb Al+++ ADDED/lb P IN PRI. EFF.)
⊙ ALUMINATE FED UNIT
△ ALUM FED UNIT


% PHOSPHORUS REMOVED ACROSS SECONDARY UNIT
94
90
86
82
78
74
70
0
0.4
0.8
1.2
1.6
2.0
2.4
ALUMINUM ION APPLICATION RATE
(lb Al +++ ADDED/lb P IN PRI EFF.)

POMONA DATA, AVERAGE VALUES

1968 DATE	CHEMICAL ADDED	AL:P RATIO WT./WT.	Phosphorus, mg/l			Percent Removal	
			PRIMARY EFFLUENT	FINAL EFFLUENT (UNFILTERED)	FINAL EFFLUENT (FILTERED)	UNFILTERED	FILTERED
2/12 - 2/26	ALUMINATE	1:1	13.2	2.6	2.1	80	83
2/26 - 3/11	ALUMINATE	1.5:1	13.2	2.3	0.9	83	94
3/18 - 4/1	ALUM	1.1:1	12.8	2.7	2.2	79	83
4/1 - 4/15	ALUM	1.4:1	13.5	1.4	0.7	90	95
4/15 - 4/29	ALUM	1.8:1	13.8	1.5	0.3	89	98
5/13 - 5/27	ALUMINATE	1.5:1	13.2	2.4	1.4	82	90

SIDE EFFECTS OF ALUMINUM ADDITION

ALUMINATE

1. NATURAL BUFFER.
2. EVERY LB ALUMINUM ADDED ALSO ADDS 0.85 LB SODIUM TO SYSTEM.

ALUM

1. USES UP ALKALINITY
2. MAY REQUIRE CHEMICAL BUFFER.
3. EVERY LB ALUMINUM ADDED ALSO ADDS 5.3 LB SULFATE TO SYSTEM.

EXAMPLE OF SIDE EFFECTS FROM PILOT PLANT STUDY

	ALUMINATE DOSED UNIT	ALUM DOSED UNIT
AVG. Al ADDED - mg/l	14.8	13.4

	PRI. EFF. mg/l	FINAL EFF.-ALUMINATE DOSED UNIT mg/l	FINAL EFF.-ALUM DOSED UNIT mg/l
Na	51	62	49
SO_4	130	114	190

SLUDGE SORPTION:

Na : 51 - 49 = 2 mg/l

SO_4: 130 - 114 = 16 mg/l

MEASURED Na ADDED BY ALUMINATE =

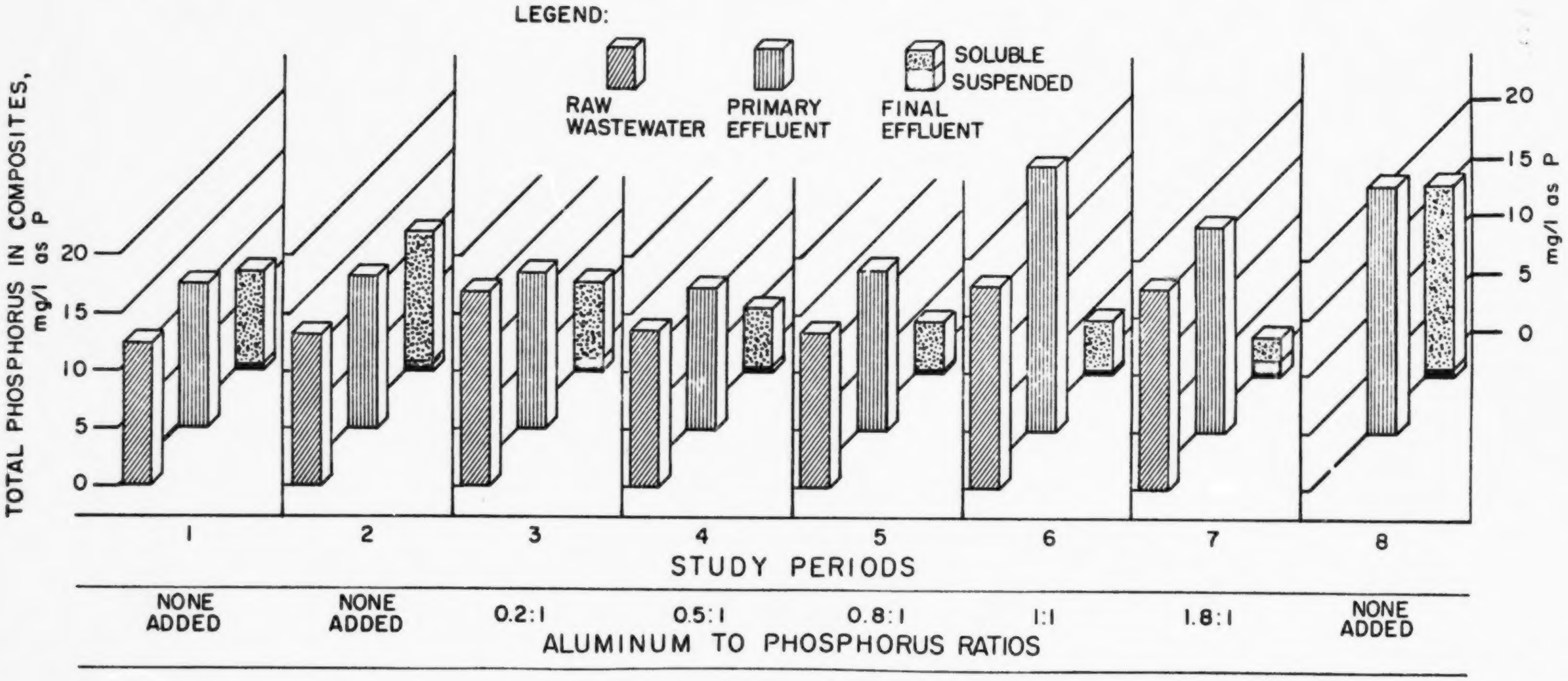
(62 - 51) + 2 = 13 mg/l

THEORETICAL Na ADDED = 14.8 x 0.85 = 12.6 mg/l

MEASURED SO_4 ADDED BY ALUM =

(190 - 130) + 16 = 76 mg/l

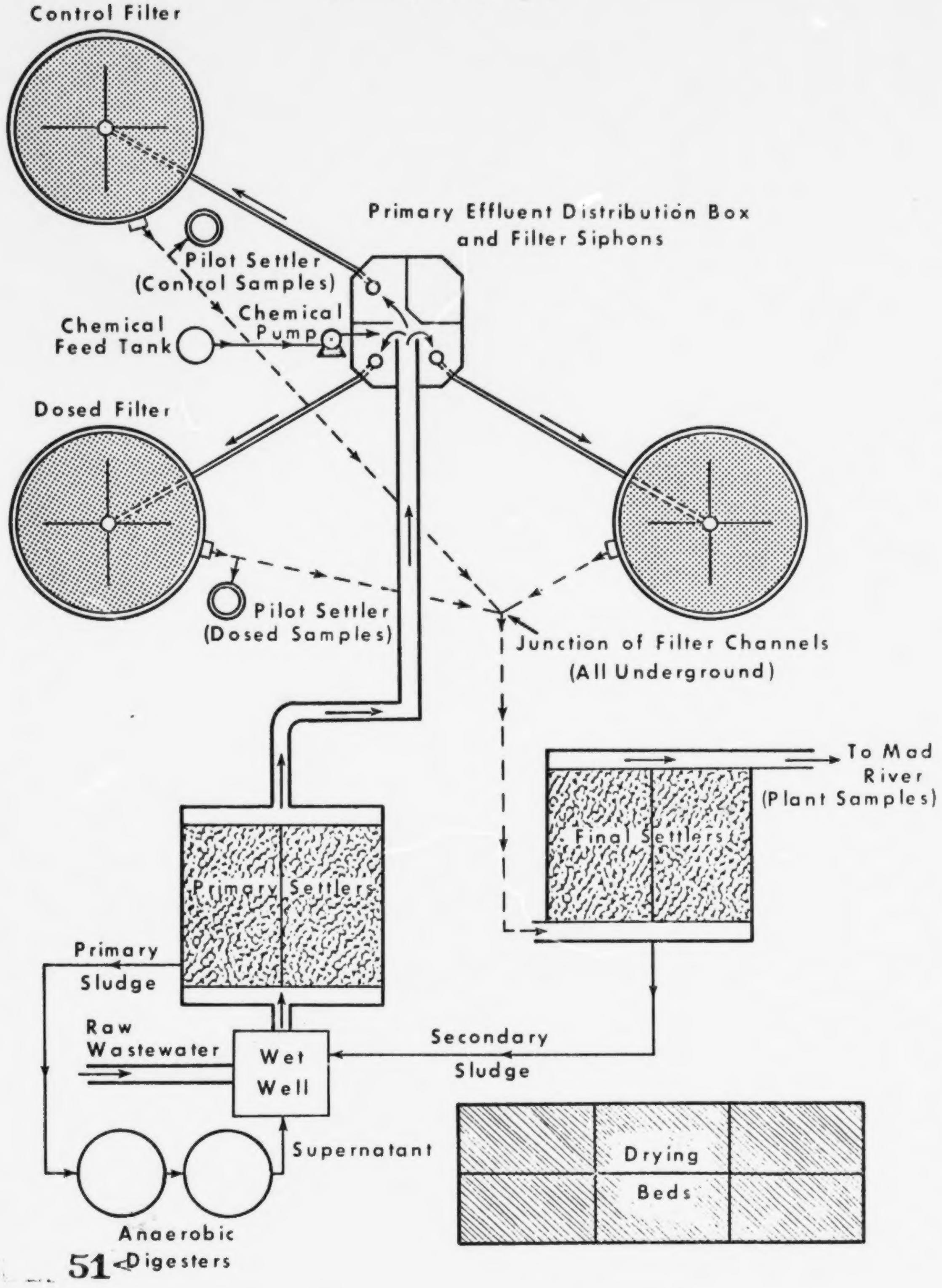
THEORETICAL SO_4 ADDED = 13.4 x 5.3 = 71 mg/l



LITTLE MIAMI TREATMENT PLANT (1 mgd)

AVERAGE PHOSPHORUS VALVES FOR 5-DAY PERIODS

- FAIRBORN, OHIO TRICKLING FILTER PLANT
Schematic Diagram


Control Filter
Primary Effluent Distribution Box
and Filter Siphons
Pilot Settler
(Control Samples)
Chemical
Pump
Chemical
Feed Tank
Dosed Filter
Pilot Settler
(Dosed Samples)
Junction of Filter Channels
(All Underground)
To Mad
River
(Plant Samples)
Final Settlers
Primary Settlers
Primary
Sludge
Raw
Wastewater
Wet
Well
Secondary
Sludge
Supernatant
Drying
Beds
Anaerobic
Digesters

FAIRBORN, OHIO TRICKLING FILTER
(Percent Removals)

Unit efficiency - Primary effluent to final effluent

	Total Phosphorus	COD	S. S.	pH Mode	Al : P
Dosed Filter	63	74	51	7.9	1 : 1
Control Filter	13	75	51	7.8	--

Overall efficiency - Raw waste water to final effluent

	Total Phosphorus	COD	S. S.	pH Mode	Al : P
Dosed Filter	64	83	84	7.9	1 : 1
Control Filter	17	83	85	7.8	--
Entire Plant	37	84	92	7.6	0.3 : 1

BULK DELIVERED CHEMICAL PRICE STRUCTURE
FOR PROJECTING PHOSPHORUS REMOVAL COSTS

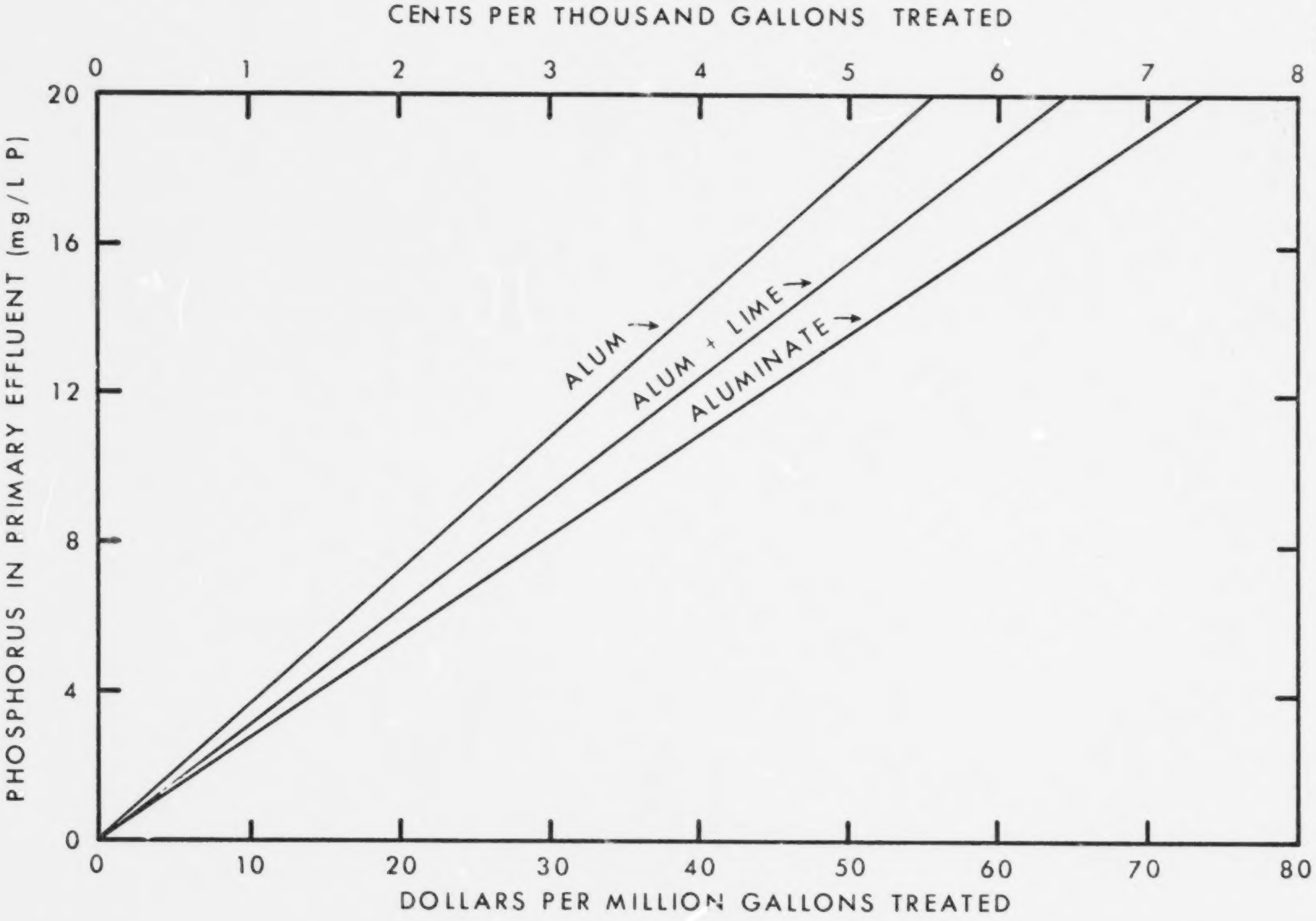
ALUMINUM SULFATE (FREIGHT EQUALIZED)
1. LIQUID - 1.22 cents/lb. as ALUM
27.7 cents/lb. as Al^{+++}

2. DRY - 2.87 cents/lb. as ALUM
30.8 cents/lb. as Al^{+++}

SODIUM ALUMINATE (DELIVERED TO SOUTHWEST OHIO)
1. DRY - 12.66 cents/lb. as ALUMINATE
36.7 cents/lb. as Al^{+++}

2. LIQUID - 6.42 cents/lb. as ALUMINATE
42.5 cents/lb. as Al^{+++}

QUICKLIME (CaO) - 1.15 cents/lb.
(DELIVERED TO SOUTHWEST OHIO)



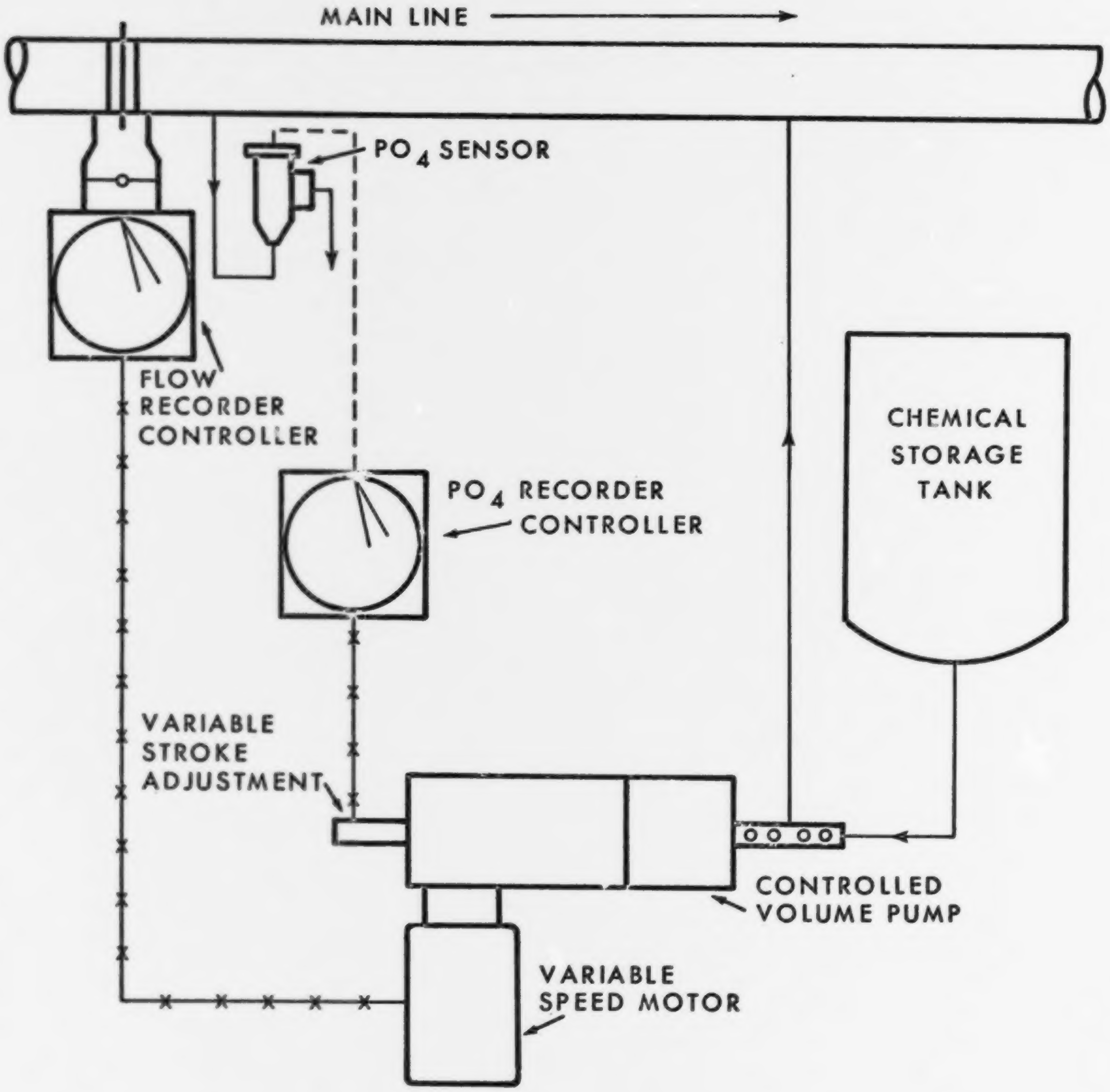
CHEMICAL COST FOR 90% PHOSPHORUS REMOVAL

CHEMICAL COSTS OF REMOVING PHOSPHORUS
BY MINERAL ADDITION

BASIS:

1. PRIMARY EFFLUENT PHOSPHORUS = 10 mg/l as P.
2. EVERY 5 mg/l ALUM ADDED (as Al^{+++}) USES UP 34 mg/l ALKALINITY (as $CaCO_3$).
3. FOR 80% PHOSPHORUS REMOVAL, Al/P = 1/1 BY WEIGHT.
4. FOR 90% PHOSPHORUS REMOVAL, Al/P = 1.2/1 BY WEIGHT.

	ALL COSTS IN DOLLARS PER MILLION GALLONS TREATED	
	80% REMOVAL	90% REMOVAL
LIQUID ALUM	23	28
DRY ALUM	26	31
LIQUID ALUM + LIME	27	32
DRY ALUM + LIME	29	35
DRY ALUMINATE	31	37
LIQUID ALUMINATE	36	43



MAIN LINE
PO$_4$ SENSOR
FLOW RECORDER CONTROLLER
PO$_4$ RECORDER CONTROLLER
CHEMICAL STORAGE TANK
VARIABLE STROKE ADJUSTMENT
CONTROLLED VOLUME PUMP
VARIABLE SPEED MOTOR

DUAL AUTOMATIC OPEN LOOP
CHEMICAL FEED SYSTEM FOR CONTROLLED DOSING

- TOTAL TREATMENT COSTS -
ACTIVATED SLUDGE TREATMENT
PLUS PHOSPHORUS REMOVAL

COSTS IN DOLLARS PER MIL GAL TREATED

	PLANT SIZE - MGD		
	1	10	100
CURRENT ANNUAL OPERATING COSTS FOR CARBON AND SOLIDS REMOVAL INCLUDING DEBT RETIREMENT	190	120	70
CHEMICAL COST FOR 90% PHOSPHORUS REMOVAL USING LIQUID ALUM - INFLUENT PHOSPHORUS = 10 mg/1 P	28	28	28
ADDITIONAL DEBT RETIREMENT AND O & M COSTS FOR PHOS. REMOVAL (ESTIMATED)	15	5	1
TOTAL INCREMENTAL COSTS FOR PHOSPHORUS REMOVAL	43	33	29
TOTAL ANNUAL OPERATING COSTS FOR CARBON, SOLIDS AND PHOSPHORUS REMOVAL (ESTIMATED)	233	153	99
% INCREASE IN TREATMENT COSTS FOR PHOSPHORUS REMOVAL (ESTIMATED)	23	28	42

PHOSPHORUS REMOVAL BY TERTIARY TREATMENT WITH LIME AND ALUM

Carl A. Brunner

I. Lime Treatment of Secondary Effluent

A. Theory

1. Phosphorus Removal

In well treated secondary effluent most of the phosphorus is available as orthophosphate. During lime treatment this is removed by precipitation with calcium ion as a form of calcium phosphate, probably as hydroxyapatite. The reaction for hydroxyapatite formation is:

$$5\ Ca^{++} + 3\ HPO_4^{=} + 4\ OH^- \rightarrow Ca_5\ OH(PO_4)_3 \downarrow + 3\ H_2O \qquad (1)$$

It can be seen from this equation that the precipitation of hydroxyapatite is strongly pH dependent, with solubility decreasing as pH increases. It will be shown later that this pH dependence is significant in phosphate removal from wastewater.

Other forms of phosphorus are removed by incorporation in, or adsorption on, floc particles that form during lime treatment.

2. Other Reactions Taking Place

There are a number of ions in wastewater that enter into reactions during lime treatment making the chemistry of the process complex. Although these reactions do not directly involve any of the various forms of phosphorus, they do effect lime dose and ease of carrying out lime treatment.

The principal reaction is the formation of calcium carbonate from bicarbonate alkalinity in the water. This can be pictured as taking place in two ways as follows:

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2\ CaCO_3 \downarrow + 2\ H_2O \qquad (2)$$

$$NaHCO_3 + Ca(OH)_2 \rightarrow CaCO_3 \downarrow + NaOH + H_2O \qquad (3)$$

In these equations lime is shown as the hydroxide. Generally, lime is available as calcium oxide and must be slaked before use. From these equations it can be observed that two moles of calcium carbonate may form per mole of calcium hydroxide entering into the reaction if sufficient calcium is already present in the water. If the water is very low in calcium content, a situation represented by equation 3, as little as one mole of calcium carbonate may be all that can form per mole of calcium hydroxide. Since it appears from data obtained at the Joint FWPCA-D.C. Pilot Plant, Washington, D. C., that the settleability of lime treatment sludge improves with increasing calcium carbonate content, the bicarbonate and calcium concentrations are significant factors in determining how well lime treatment will perform. It is true that lime dose increases with increasing bicarbonate alkalinity, but this disadvantage is overshadowed by the advantage of more rapid sludge settling.

Since the conversion of HCO_3^- to $CO_3^=$ is pH dependent, the precipitation of $CaCO_3$ is also pH dependent. At a pH of about 10, conversion to CO_3 is essentially complete. From consideration of the solubility product for $CaCO_3$ this can be seen to be the pH at which Ca solubility will be minimum.[3] This is an important point if the water being treated has a high initial calcium content, the condition shown in equation 2, and if removal of calcium hardness is of interest. Adding lime to increase the pH above 10 will result in increased calcium content since there is very little $CO_3^=$ left for further $CaCO_3$ precipitation.

If the pH is increased to about 11 or above, magnesium is precipitated as follows:

$$Mg^{++} + 2\ OH^- \rightarrow Mg(OH)_2 \downarrow \qquad (4)$$

This reaction has the beneficial effect of producing a flocculant precipitate that improves removal of suspended solids. Substantial additional lime may be required, however, to reach the required high pH.

One reaction that should not be ignored is the conversion of ammonium ion to uncharged ammonia:

$$NH_4^+ + OH^- \rightarrow NH_3 + H_2O \qquad (5)$$

At a pH of 7, NH_4^+ is the predominant form. As the pH is increased the amount of NH_3 increases. The reaction results in a lime demand. This is not a detrimental reaction if ammonia removal by air stripping is included in the system. In that case NH_4 must be converted to NH_3 before removal will occur.

B. Systems

1. Single-stage treatment

Single-stage treatment refers to treatment in which the water is maintained at essentially a single pH value from the time lime is added until the water leaves the treating equipment. In single-stage treatment sufficient lime slurry to reach the desired pH is mixed with the water. Precipitation by reactions discussed earlier occurs. Time is allowed for precipitate particles to flocculate to a size that settles rapidly. The floc is then settled and the supernatant water is either discharged directly or passed through a sand or multi-media filter to improve solids removal. The pH that would be selected for treatment would be the lowest that gives satisfactory phosphate removal, possibly as low as 9.5.

Since single-stage treatment requires a minimum of equipment, it is the most likely mode to be used where phosphorus removal is the primary objective. It may not be feasible, however, to use single-stage treatment in all locations. Where bicarbonate alkalinity is very low, good settling may not occur because of insufficient calcium carbonate as a weighting agent. In these cases carbonate ion could be supplied by adding sodium carbonate as is done in lime-soda softening or by adding carbon dioxide. It may be more practical, however, to utilize two-stage treatment.

The sludge from the settler must be further treated for disposal. In many cases calcination of the sludge to recover lime may be practical.

2. Two-Stage Treatment

Two-stage treatment is used frequently in softening of municipal water supplies. There is a full two-stage process and a split feed process. The full two-stage process will be described here. In a typical two-stage process, sufficient lime is mixed with the water to raise the pH to 11 or above. At this pH most of the magnesium hardness is removed as shown by equation 4, but calcium hardness remains high. Precipitates that are formed are settled and the water is passed to a second stage after having been contacted with CO_2. Sufficient CO_2 is used to reduce the pH to about 10 and to cause removal of calcium as $CaCO_3$. The water from the second stage of treatment can be discharged directly if the suspended solids concentration is acceptable or passed through a filter.

Two-stage treatment for phosphorus removal would be carried out similarly to softening. Precipitation of phosphate would occur in the high-pH stage. Since the reason for using two-stage treatment would probably be poor floc settleability, considerable precipitated phosphorus would be expected to be carried over to the second stage. The dense calcium carbonate precipitate formed in the second stage when mixed with the light floc should produce a well settling sludge. The water leaving the second stage should, therefore, be low in phosphate content. Preliminary studies at the Joint FWPCA-D.C. Pilot Plant indicate improved settling in the first stage may be possible if high $CaCO_3$ sludge from the second stage is added to the floc in the first stage.

Sludge from the two settlers may be calcined to recover lime. The sludge from the second stage having a high $CaCO_3$ content should produce high quality lime.

C. Equipment

Not enough studies have been made to determine what types of equipment are best suited for lime treatment of wastewater. Upflow clarifiers designed for lime softening of surface and well waters, and containing mixing and flocculating zones at the center of a circular settler have been found satisfactory, although not necessarily optimum. These can be operated with or without a sludge blanket at settler upflow rates of 1 gpm/ft^2 or higher. A feature that has generally been included in the equipment is solids contact, i.e., a mechanism for circulating part of the sludge from the settling area back to the mixing or flocculating zones. The objective of contacting sludge with feed water is to encourage new precipitate to form on the already formed sludge particles rather than as separate particles. The result is larger particle size and more rapid settling. Sludge may be circulated internally by proper design of the equipment. Better control of the amount of sludge recycled can be obtained by withdrawing the sludge from the settler through an external pipe and pumping it back to the mixing or flocculating zones.

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Longitudinal flocculation-settler systems may also be useful for lime treatment of wastewater. Little or no work has been done with this equipment on wastewater. It is not as convenient to use with solids contact as the upflow systems.

Filtration can be carried out with sand or multi-media filters. With dual-media filters of anthracite coal and sand, operation at rates of 2 gpm/ft^2 are easily obtainable. Somewhat higher rates can probably be expected if good control is maintained on turbidity of the water from the settler.

Novel filtration devices that replace the conventional clarifier and filter have been or are being tested. These may be practical for lime treatment. Further work as required before these devices can be recommended for plant-scale installations.

D. Results of Pilot Scale Studies

1. Description of conditions and Equipment

Two pilot studies, one at the Lebanon, Ohio Pilot Plant and one at the Joint FWPCA-D.C. Pilot Plant, cover the extremes of conditions that may be met when treating secondary effluent.

The effluent at Lebanon is from a conventional activated sludge plant. The water has calcium concentrations as high as 100 mg/l and bicarbonate alkalinities sometimes exceeding 400 mg/l as $CaCO_3$. It can be treated effectively in a single-stage process. Figure 1 shows the 75-gpm upflow clarifier used for the study. The equipment is designed to operate with internal circulation of sludge into the mixing zone. External recycle of sludge has also been used. Upflow rate in the settling zone is 1 gpm/ft^2. Detention time in the clarifier is 110 minutes. Following the clarifier are dual-media filters containing 6 in. of 0.46-mm sand overlaid with 18 in. of 0.75-mm anthracite coal. Filtration rate is 2 gpm/ft^2.

The effluent at the Washington, D. C. plant is from a high rate activated sludge plant and has higher soluble organic content and suspended solids than would be obtained from a conventional activated sludge plant. The calcium concentration is about 40 mg/l and the alkalinity is in the range of 100 to 150 mg/l as $CaCO_3$. This water does not produce a rapidly settling floc and cannot be treated in a single-stage process unless carbonate is supplied in a form such as Na_2CO_3. The water can be treated in a two-stage system with carbonation before the second stage. This study is being conducted using upflow clarifiers only slightly different from the Lebanon unit. Flow to the clarifiers is 50 gpm for a settler rate of 1 gpm/ft^2. Sludge is circulated externally to provide solids contact. Dual-media filters following the second stage clarifier are essentially the same as at Lebanon. The filters are operated at about 3.5 gpm/ft^2.

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2. Phosphorus Removal

Removals of total phosphorus achieved in the Lebanon study are shown in Figure 2 for the clarifier effluent and in Figure 3 for the filter effluent. Average concentration of phosphorus in the feed was 30 mg/l as PO_4. The reduction in phosphorus concentration with increasing pH is clearly shown in the filter effluent. The effect of pH is not as obvious in the clarifier effluent because of the presence of suspended solids containing precipitated phosphate. At a pH of 9.5 the clarifier effluent contained about 15 mg/l of largely inorganic suspended solids. Filtration removed the solids effectively resulting in water with turbidity usually less than 1.0 JTU and often less than 0.2 JTU. Average filter run length was about 100 hours. Because of the carry-over of phosphorus in suspended solids, phosphorus removal using a clarifier alone is dependent on settler upflow rate. At the 1-gpm/ft^2 rate used in this study, 90 percent phosphorus removal was obtained at a pH as low 9.7. Better results should be achieved if the upflow rate is decreased. With filtration, 90 percent phosphorus removal was obtained at a pH of 9.5 and much greater removals were possible as pH increased.

In the Washington, D. C. study removals of phosphorus down to 2 mg/l as PO_4 were possible operating with one clarification stage and a filter, and with addition of at least 100 mg/l of Na_2CO_3 to the clarifier. Sufficient lime was required to raise the feed pH above 11.5 where formation of flocculent $Mg(OH)_2$ improved clarification. The cost of the Na_2CO_3 in this case is too high to justify this mode of operation rather than two-stage treatment. Preliminary runs indicate it may be possible to replace most of the Na_2CO_3 with CO_2, but further work is required to demonstrate dependable operation.

Two-stage operation followed by filtration at Washington gives slightly less than 90 percent phosphorus removal and produces water with concentration of about 2 mg/l as PO_4. The first stage is operated at a pH of least 11.7 and the second stage is operated at a pH between 9.5 and 10.0. Phosphorus concentration in the effluent from the second-stage clarifier is only slightly higher than in the filter effluent. The suspended material is very fine and is not effectively removed by the filters. In this case, decrease in settler upflow rate probably would not significantly improve phosphorus removal. Improved removal of suspended material and, therefore, improved phosphorus removal can be obtained in the filter by adding ferric ion as a flocculating aid.

3. Lime and Other Chemical Requirements

Minimum lime dose should be the sum of the lime requirements of reactions discussed earlier. If the necessary data on water composition were available, the lime requirement could be calculated. These requirements probably would not represent the total lime dose because some unused lime becomes occluded in floc particles. It is possible that organic materials in the wastewater also affect lime requirements.

In the Lebanon study an approximate relation was found between feed alkalinity, clarifier pH, and lime dose. Results for two values of alkalinity and pH are given in Table 1. It is estimated that operation at a pH of 9.5 could be carried out at Lebanon with an average lime dose of 250 mg/l as $Ca(OH)_2$.

Although the alkalinity of the water in the Washington study is much lower than at Lebanon, the need for high pH in the first stage results in a lime requirement of over 400 mg/l as $Ca(OH)_2$.

Recarbonation to produce $CaCO_3$ in the second stage of a two-stage process requires appreciable amounts of CO_2. If calcination of sludge for lime recovery is included in the system, adequate CO_2 should be available. If sludge is not calcined, CO_2 would probably be produced by burning a cheap source of fuel. The amount of CO_2 required is approximately that necessary to combine with the calcium in the first stage effluent. Inefficiencies in the CO_2 absorption system would increase the requirements.

Various flocculent aids may be useful for improving solids removal, especially when filtration is included in the treatment system. Little experience is available concerning the best types of material or concentrations required.

4. Sludge Characteristics

Since the lime sludge from a clarifier must be concentrated for calcination, or in some other way treated for disposal, its dewatering characteristics are important.

Lime sludge containing a large amount of $CaCO_3$ is quite granular and can be dewatered easily. The sludge from the Lebanon clarifier has these characteristics. Although it is removed as a 3-percent slurry, it could be allowed to thicken to a much higher concentration if there were a mechanical scraper in the bottom of the clarifier. At present thickening is carried out in a separate tank. The solids thicken rapidly to a 15-percent slurry which is conducted to drying beds. If calcination were included in the system, the slurry would be further concentrated in a centrifuge or on a vacuum filter. The sludge will dewater to 50 percent solids on the drying beds even at times of the year when evaporation is not significant. Similar results could probably be obtained using a centrifuge or filter.

In a two-stage system, sludge from the second stage should thicken well because it is mostly $CaCO_3$. Thickening characteristics of the sludge from the first stage will vary depending upon water composition. For a water such as that at Washington, D. C., sludge does not thicken well in the first stage. It contains significant amounts of biological solids and $Mg(OH)_2$ which have a flocculent nature. The combined sludges from the two-stages are dewatered on a vacuum filter. Available results indicate the sludge will dewater to about 30 percent solids.

TABLE 1. LIME REQUIREMENTS

Feed Water Alkalinity (mg/l as $CaCO_3$)	Clarifier pH	Approximate Lime Dose (mg/l of $Ca(OH_2)$
300	9.5	200
300	10.5	350
400	9.5	300
400	10.5	500

5. Operating Problems

At Lebanon the only significant problem has been post precipitation of $CaCO_3$. This is especially severe in cold weather. The result is calcification of the filter media. Control of pH also becomes more difficult because of scale formation on the electrodes. Precipitation on the filters can be prevented by reducing the pH of the clarifier effluent after it has left the clarifier. At Lebanon this was accomplished with sulfuric acid. On plant scale CO_2 would probably be used.

At Washington inability to form a dense floc in a single-stage system or in the first stage of a two-stage system has been the most serious problem. The result is high suspended solids concentration in the clarifier effluent. Occasionally very large amounts of suspended material are found in the effluent. A second treatment stage acts as a valve to prevent the excess solids from escaping with the product water. A more satisfactory solution is desirable. New concepts in equipment design may be useful when settling of sludge is a problem.

At both Lebanon and Washington, poorer settling is encountered in cold weather. This is typical of clarification processes.

E. Economics

Without long-term operating experience it is impossible to estimate accurately the cost of lime treatment. In Table 2 are given some approximate cost figures based on the stated assumptions. The cost for two-stage treatment as significantly higher than the cost for single-stage treatment. It is likely that, where single-stage treatment is applicable, the required lime dose will be substantially less than the assumed 350 mg/l. The difference between single-stage and two-stage treatment may, therefore, be greater than the table indicates. The cost of lime, 2.04¢/1,000 gal. for the chosen dose and purchase price, is a significant fraction of the total operating cost for all plant sizes, and for very large plants becomes the dominant cost. The same cost has been assumed for purchased lime as for lime calcined from sludge. This is likely to be true for large plants. For plants smaller than 10 mgd, however, calcination of sludge is likely to be more expensive than purchased lime. The cost of alternate means of sludge disposal would have to be considered in these cases. Where sludge disposal is expensive calcination may be practical down to very small plant sizes.

The cost of filtration for all plant sizes is substantial compared to clarification. In many cases filtration should not be required when phosphorus removal is the objective. Even when high suspended solids concentrations in clarifier effluent are a problem, increasing settler area may be cheaper than filtration. Filtration would be necessary where high clarity water is desired.

TABLE 2. COST OF LIME TREATMENT

Type of Treatment	Cost (¢/1,000 gal.)		
	Plant Size (mgd)		
	1.0	10	100
Single Stage Without Filtration	6	4	3
Two Stage Without Filtration	9	5	4
Filtration	6	3	1.5

Assumptions:

Upflow clarifiers and dual media filters
Equipment amortized over 25 years at 4 1/2% interest
Settler overflow rate-1,000 gpd/ft^2
Lime dose - 350 mg/l as $Ca(OH)_2$
Lime cost - \$18.50/ton of CaO
Cost of dewatering sludge and calcining - \$18.50/ton of CaO produced

II. Alum Treatment of Secondary Effluent

A. Theory

Orthophosphate removal under pH conditions of most secondary effluents is probably largely by precipitation as $AlPO_4$. Phosphate may also be removed by incorporation in a complex along with aluminum and hydroxyl ions or by adsorption on the aluminum hydroxide flox formed by reaction of aluminum with alkalinity in the eastewater.

Removal of other forms of phosphorus may occur by adsorption on, or incorporation in, $Al(OH)_3$ floc.

B. Equipment

Removal of phosphorus with alum can be carried out essentially the same as alum clarification using upflow or longitudinal clarifiers with or without a filter. Very little information is available to judge what type of equipment is best. Because the aluminum dose needed to produce a filterable floc may be substantially less than that to produce a settleable floc, novel filters with high solids capacity may be useful in this application.

C. Feasibility of the Process

Enough studies have been carried out to show that phosphorus removal by alum treatment is technically feasible. Unless, however, special treatment equipment can be devised or an inexpensive method can be found to recover aluminum ion from the sludge formed during treatment, the cost is not likely to be as low as the cost for lime treatment. The high cost of this treatment method results from both the expense of the alum, and from the expense of sludge disposal.

If it were possible to remove phosphorus as $AlPO_4$, approximately 100 mg/l of commercial alum would be required for 10 mg/l phosphorus. Since some aluminum is consumed in $Al(OH)_3$ formation, the actual alum dose will be higher. Experimental results suggest that about two moles of aluminum may be required per mole of phosphorus in conventional clarification equipment. Using the two-to-one ratio, about 200 mg/l of alum would be necessary. The cost of the alum would be between 4 and 5¢/1,000 gal.

Experimental results indicate that the sludge from an alum clarifier is likely to contain only about 0.5 percent solids and will dewater very slowly. Costs for concentrating the sludge and disposing of it so that it will not again contaminate the environment will, therefore, be high.

Since the cost for the alum necessary to remove phosphorus from wastewater in conventional clarification equipment is at least 2¢/1,000 gal. higher than the cost of lime for single-stage lime treatment, alum treatment could not compete with the single-stage lime process even if alum sludge disposal cost were small. For large two-stage lime treatment plants this conclusion is also true. For two-stage plants of 1 mgd or less, where costs associated with equipment become high compared to chemical costs, alum treatment would probably be competitive if sludge treatment and disposal costs were very low. Since very few locations would be suitable for disposal of the sludge at the required low cost, the overall expense of alum treatment would, in essentially all cases, be higher than lime treatment.

Since filtration gives the greatest phosphate removal for a given chemical dose, special filtration equipment that eliminates the conventional flocculator and settler may improve the economic feasibility of alum treatment. This type of equipment has not been studied sufficiently to recommend it for full-scale installations.

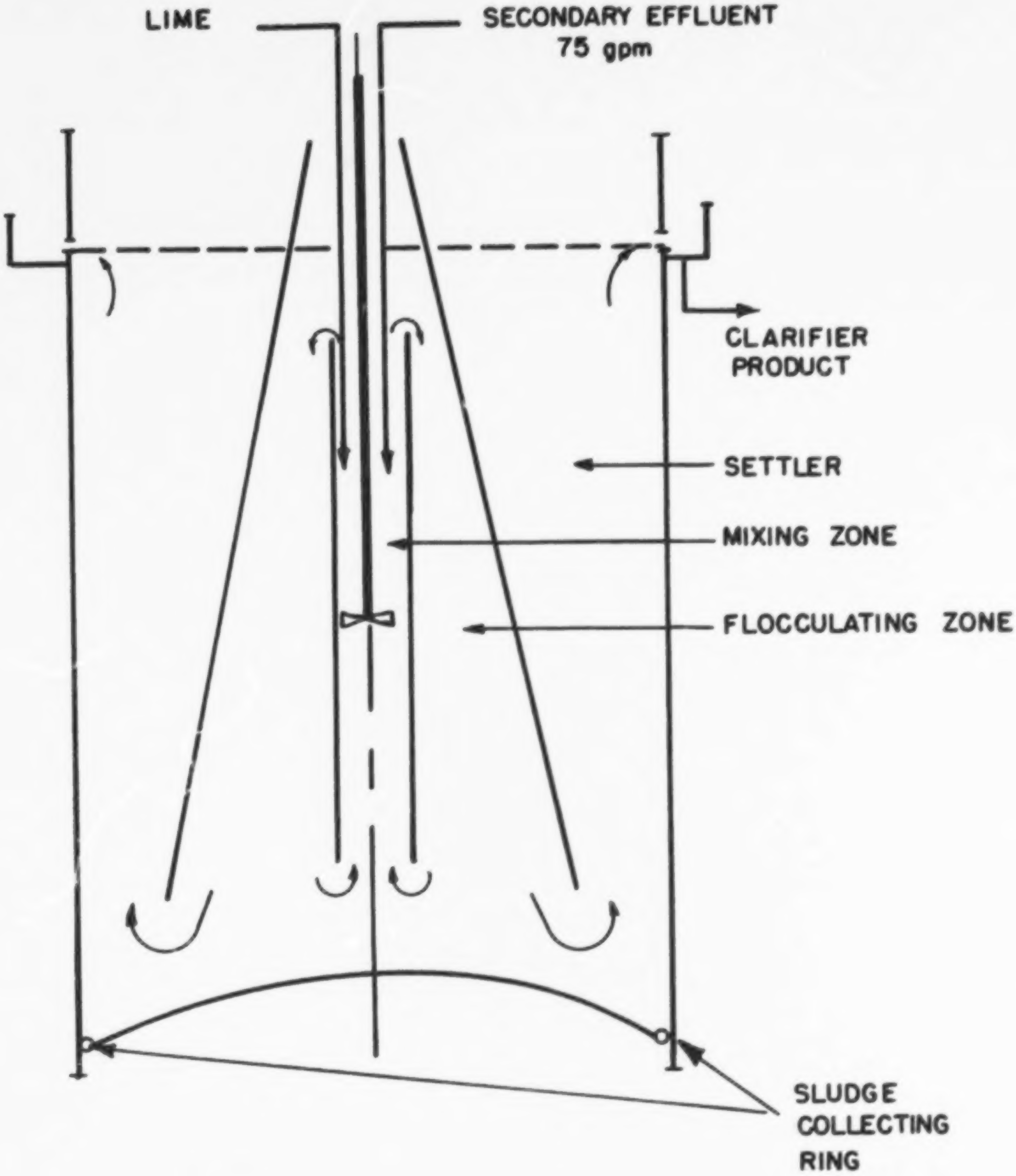
LIME
SECONDARY EFFLUENT
75 gpm
CLARIFIER PRODUCT
SETTLER
MIXING ZONE
FLOCCULATING ZONE
SLUDGE COLLECTING RING

FIGURE 1 LIME CLARIFIER

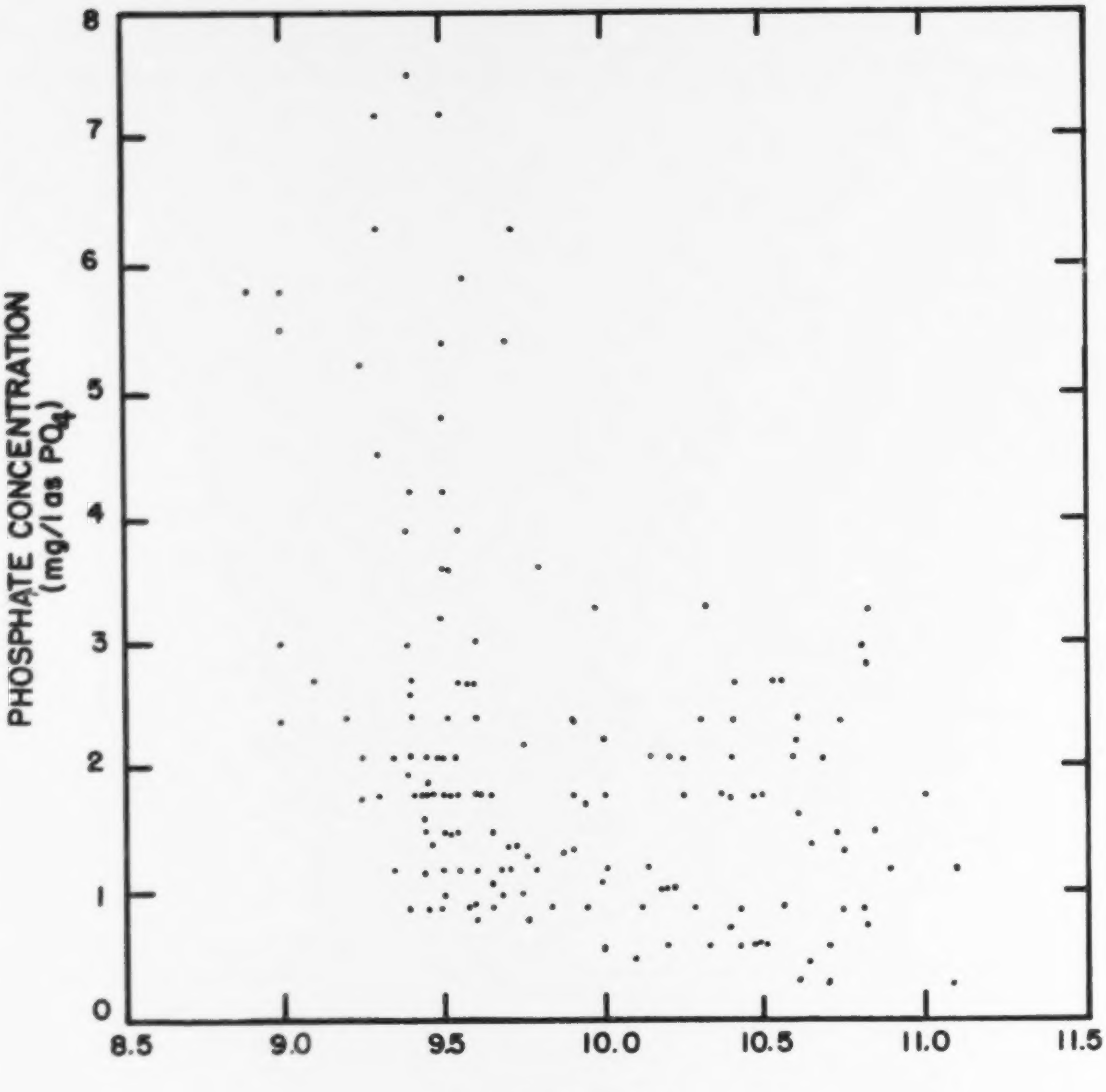

FIGURE 2. EFFECT OF pH ON PHOSPHATE CONCENTRATION OF EFFLUENT FROM LIME CLARIFIER

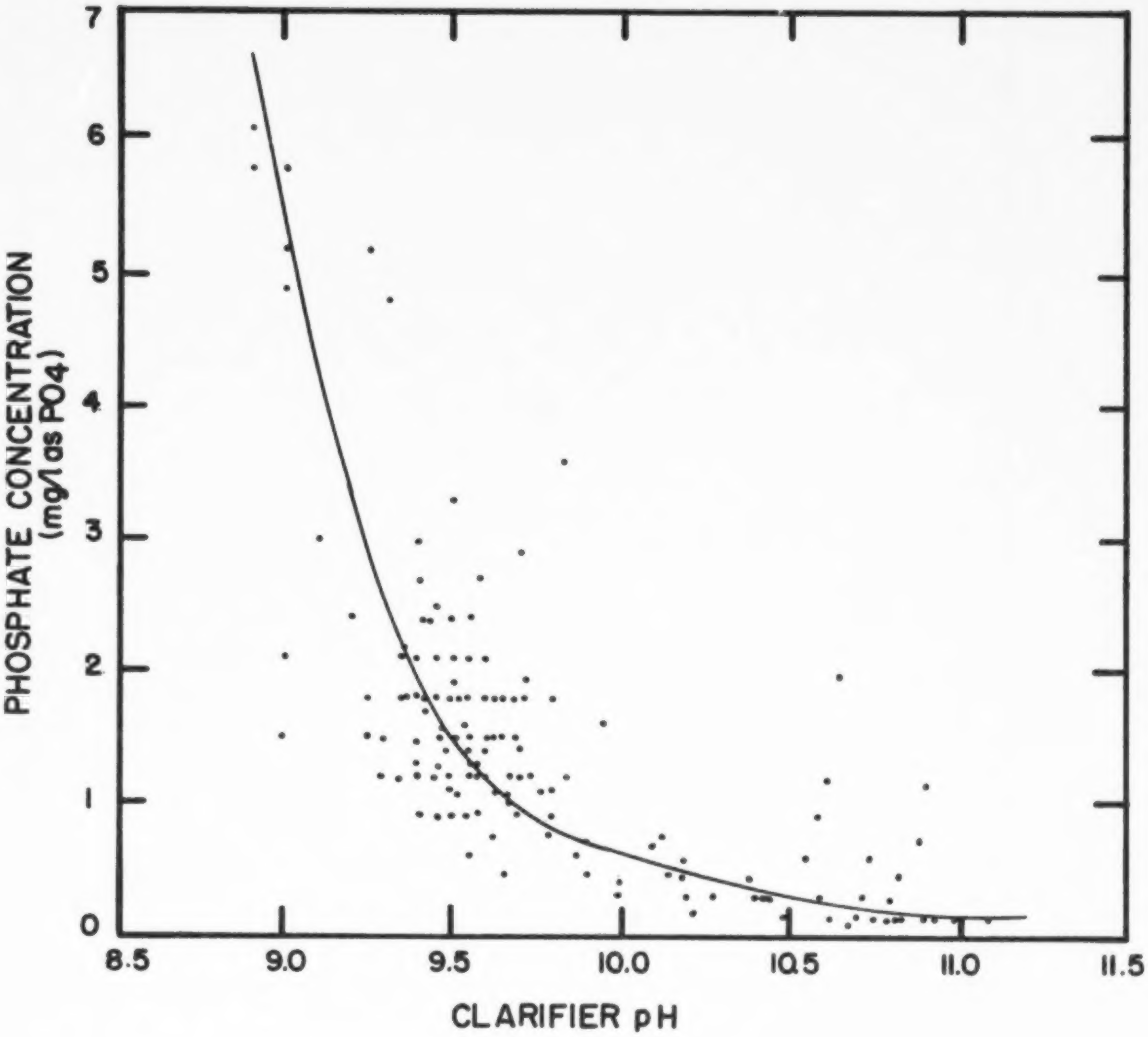

FIGURE 3. EFFECT OF pH ON PHOSPHATE CONCENTRATION OF EFFLUENT FROM FILTERS FOLLOWING LIME CLARIFIER

SECOND TECHNICAL SESSION

Oral H. Hert, Moderator

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REUSE AND DISPOSAL OF LIME AND ALUM SLUDGES
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COMBINED TREATMENT FOR REMOVAL OF BOD, PHOSPHORUS AND NITROGEN
Edwin F. Barth 2.16

PHYSICAL CHEMICAL METHODS FOR NITROGEN REMOVAL
Dr. Joseph B. Farrell 2.20

REUSE AND DISPOSAL OF LIME AND ALUM SLUDGES

Robert B. Dean

I. DISPOSAL

A. Lime removes phosphates but produces sludge.

1. Underflow 2-3% solids.
2. 250 mg/1 of $Ca(OH)_2$ produces 500-600 mg/1 of sludge.

   a. Two tons of sludge solids produced per million gallons of water.
   b. After thickening to 30% still leaves 6 tons of wet sludge.

B. Land Spreading

1. Stable, reasonable drainage.
2. Useful in agriculture in some areas.

   a. Difficult to spread thickened sludge.
   b. Can pump unthickened lime sludge in 6" pipe 1 - 25 miles. (P. V. Sanders '69)

3. May be used for soil stabilization, roads.

II. LIME REUSE

A. Chemistry

1. $Ca(OH)_2 + Ca(HCO_3)_2 \longrightarrow 2CaCO_3\downarrow + 2H_2O$

   a. pH above 9.5. Cold lime softening process.

2. $5Ca^{++} + 4OH^- + 3HPO_4^= \longrightarrow Ca_5OH(PO_4)_3\downarrow + 3H_2O$

   a. pH above 7.0 precipitates hydroxyapatite.

3. $2Ca(OH)_2 + Mg(HCO_3)_2 \longrightarrow Mg(OH)_2\downarrow + 2CaCO_3\downarrow + H_2O$

   a. pH above 10.5. $Mg(OH)_2$ is a slimy precipitate.

4. $CaCO_3 \xrightarrow{heat} CaO + CO_2$

   a. Temperature about 1800°F.

5. $CaO + H_2O \longrightarrow Ca(OH)_2$

   a. Lime slaking produces heat.

6. $Mg(OH)_2 + CO_2 \longrightarrow MgCO_3$
    - a. $MgCO_3$ is soluble cold, insoluble if warmed above 95°F.

7. $Mg(OH)_2 \xrightarrow{heat} MgO + H_2O$
    - a. MgO is insoluble in water.

B. Lime Recovery

1. Equations 4 and 5 above.
2. Practiced by Water Softening Plants.
    - a. Dayton, Ohio sells lime at $11.00 - $12.00/ton.
3. Used to make pure calcium carbonate pigment in paper mills.
4. Cost of recovery is nearly the same as cost of new lime.
    - a. Costs of waste disposal are reduced.
5. Wastewater lime treatment and recovery.
    - a. Lake Tahoe (Slechta and Culp, 1967) 7.5 MGD costs over $20/ton. Figure I.

C. Laboratory Recycle Studies. Mulbarger et al.

1. 75 liter batches. Recovered lime recycled 3 times.
    - a. See Figure II.
2. System A. Total treatment, two clarifiers with CO_2 added to adjust pH.
    - a. Maximum recovery but sludge may be hard to filter.
3. System B. A with sludge carbonated to remove $Mg(OH)_2$.
    - a. Better filterability.
4. System C. Split treatment.
5. System D. Split treatment with sludge recarbonation.
6. Lime dose. Figure III or 200 + 0.55 x Alkalinity to reach pH 11.

a. Much less required to reach pH 9.5 but clarification may be difficult in low hardness waters.

7. Phosphate recovery

a. Better than 99% in A and B. CO_2 dees not redissolve phosphates.
b. About 91% in C and D with split treatment. Time not sufficient to precipitate all of the phosphates.

8. Sludge dewatering

a. Settled 17 hours in these tests.
b. Dewater on vacuum leaf.
c. Filter yield is a function of lime dose and inerts in reused lime which greatly improve filter yield. Figure IV
d. Solids vary from 28 to 45%.
e. Must test actual water before designing dewatering equipment.

9. Sludge properties

a. Hard water; lime recovery equals needs.
b. Soft water; sludge builds up to high calcium phosphate analysis.
c. Phosphate does not leach but is available to plant roots.

10. Magnesium carbonate from recarbonation.

a. Soluble cold.
b. Precipitated by heating to 35°-40°C. (A. P. Black, personal communication)

III. ALUM SLUDGES

A. Alum or aluminate treatment of waste water.

1. Sludge contains 2Al:1P and probably Ca.

a. Also organic matter.

2. Dewatering

a. Settled sludge about 10% solids. Not thick enough for land fill.
b. Freezing improves dewatering.

3. No effect on digestion; adds bulk.
4. Land disposal may cause clogging of soil.

B. Aluminate Recovery

1. H_2SO_4 unsuitable because H_3PO_4 also dissolved.
2. $OH^- + Al(OH)_3 \rightleftarrows Al(OH)_4^-$ aluminate.
    a. Soluble and reusable.
    b. Evan $Ca(OH)_2$ removes over 50% as soluble aluminate.
3. Lime treated alum sludge can be filter pressed.
4. Incinerated sludge not expected to be a disposal problem.

Pertinent Literature

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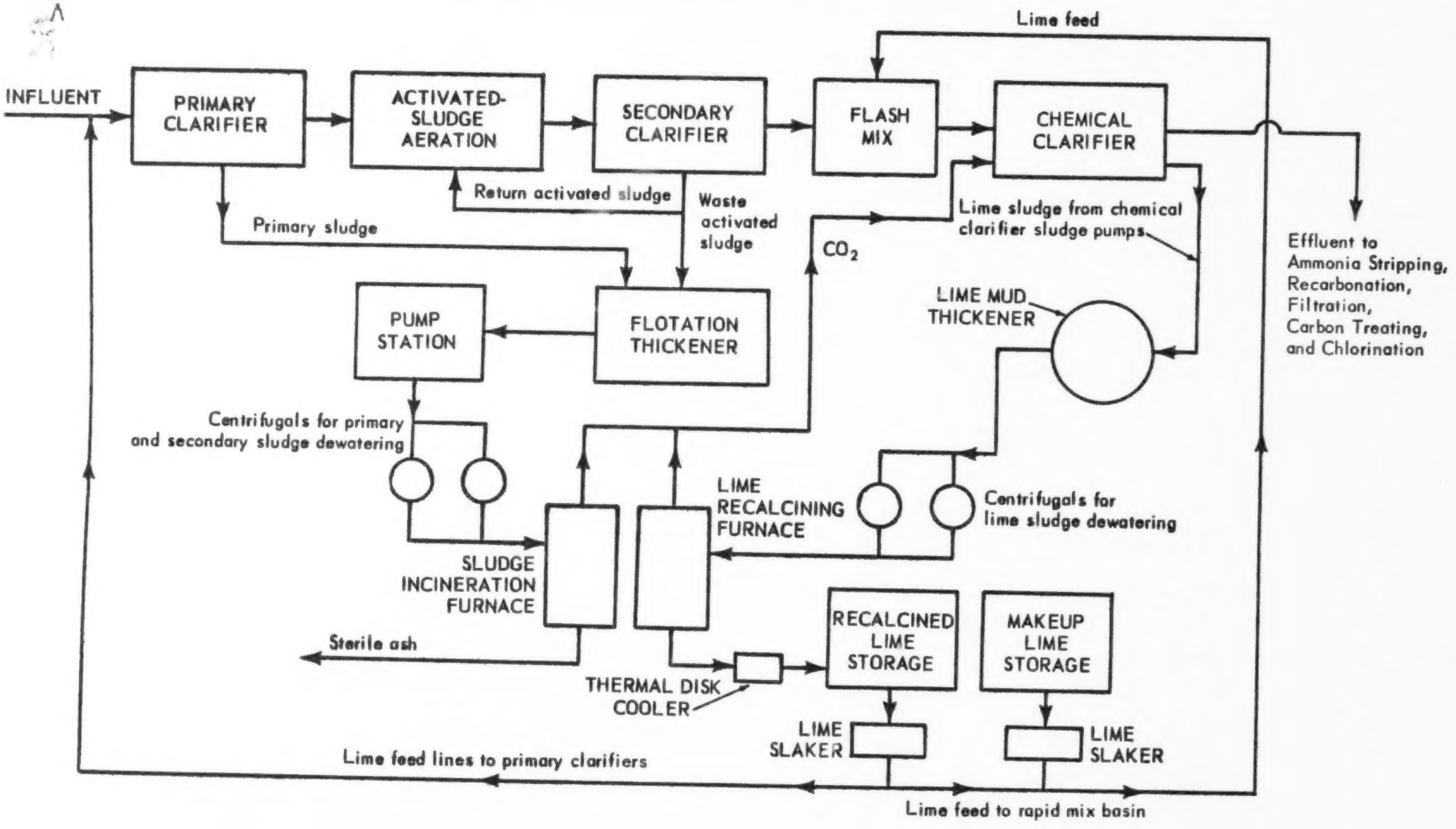
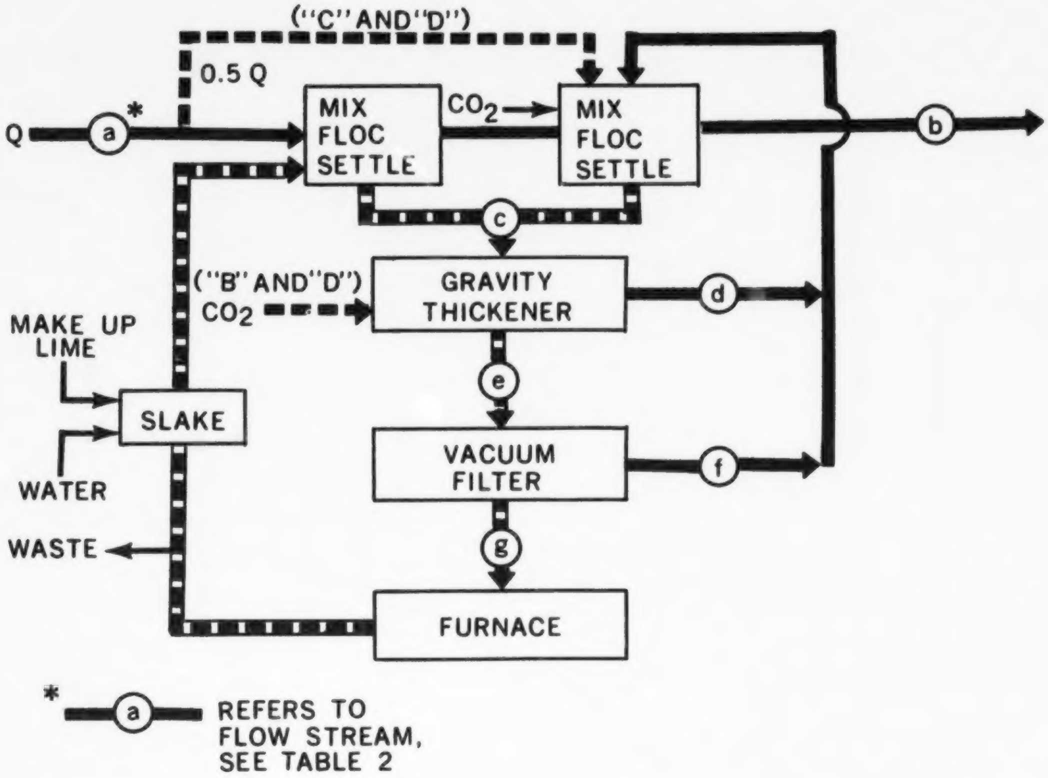
Phosphate Removal at South Lake Tahoe, with Lime Recalcination and Reuse


INFLUENT
PRIMARY CLARIFIER
ACTIVATED-SLUDGE AERATION
SECONDARY CLARIFIER
FLASH MIX
CHEMICAL CLARIFIER
Lime feed
Return activated sludge
Waste activated sludge
Primary sludge
CO$_2$
Lime sludge from chemical clarifier sludge pumps
Effluent to Ammonia Stripping, Recarbonation, Filtration, Carbon Treating, and Chlorination
LIME MUD THICKENER
PUMP STATION
FLOTATION THICKENER
Centrifugals for primary and secondary sludge dewatering
LIME RECALCINING FURNACE
Centrifugals for lime sludge dewatering
SLUDGE INCINERATION FURNACE
Sterile ash
THERMAL DISK COOLER
RECALCINED LIME STORAGE
MAKEUP LIME STORAGE
LIME SLAKER
LIME SLAKER
Lime feed lines to primary clarifiers
Lime feed to rapid mix basin

EXPERIMENTAL SYSTEMS


("C" AND "D")
0.5 Q
Q
a
*
MIX
FLOC
SETTLE
CO2
MIX
FLOC
SETTLE
b
c
("B" AND "D")
CO2
GRAVITY
THICKENER
d
MAKE UP
LIME
SLAKE
WATER
e
VACUUM
FILTER
f
WASTE
g
FURNACE
*
a

REFERS TO
FLOW STREAM,
SEE TABLE 2

SYSTEM "A"
TOTAL TREATMENT

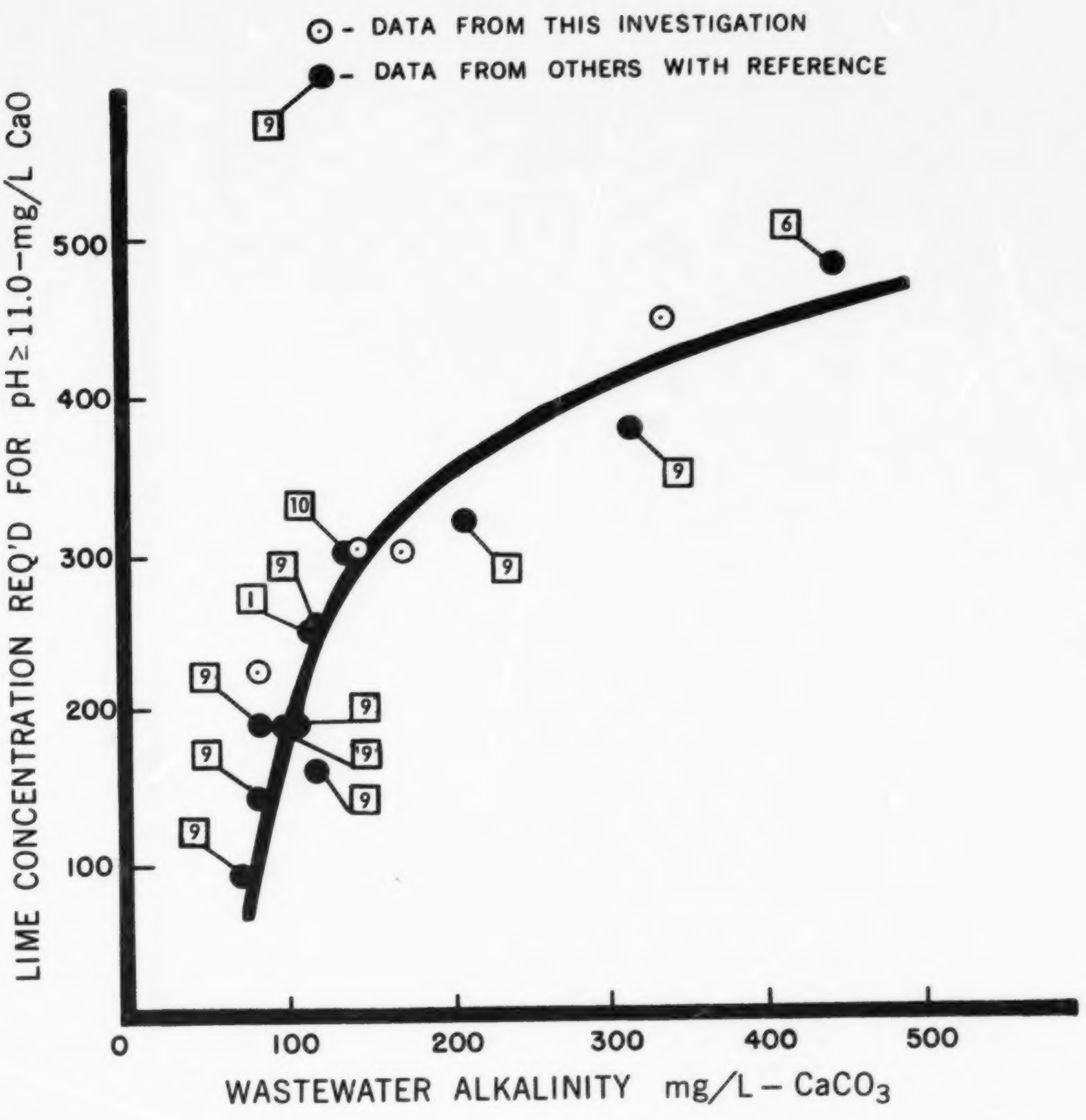
SYSTEM "B"
TOTAL TREATMENT WITH SLUDGE CARBONATION

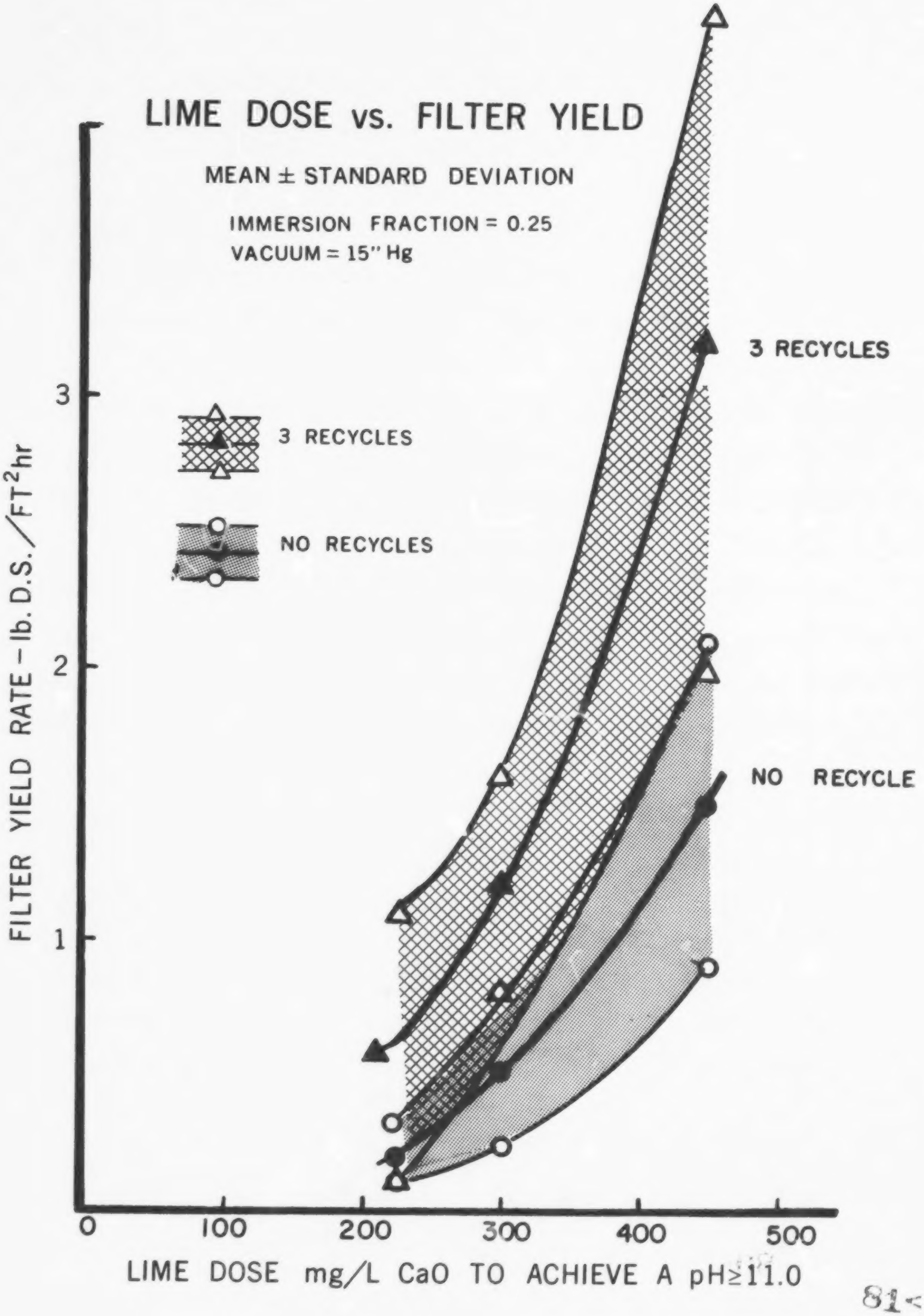
SYSTEM "C"
SPLIT TREATMENT (0.5Q to 2nd STAGE)

SYSTEM "D"
SPLIT TREATMENT WITH SLUDGE CARBONATION

NOTE: LIME DOSE FOR SYSTEMS "C" AND "D" IS ½ OF
THE LIME DOSE USED FOR SYSTEMS "A" AND "B"

LIME REQUIREMENT FOR pH≥11.0 AS A FUNCTION OF THE WASTEWATER ALKALINITY




LIME DOSE vs. FILTER YIELD
MEAN ± STANDARD DEVIATION
IMMERSION FRACTION = 0.25
VACUUM = 15" Hg
3 RECYCLES
NO RECYCLES
3 RECYCLES
NO RECYCLE
FILTER YIELD RATE – lb. D.S./FT²hr
1
2
3
0
100
200
300
400
500
LIME DOSE mg/L CaO TO ACHIEVE A pH≥11.0

ALTERNATIVE METHODS FOR PHOSPHORUS REMOVAL

Jesse M. Cohen

Preceding lectures in this workshop have described nutrient removal by biological processes, either alone or in conjunction with added inorganic precipitants. Precipitation of phosphorus with lime or with aluminum and iron salts have also been discussed and will not be repeated here. The purpose of this talk is to point out some alternative physical-chemical treatment processes for nutrient removal.

At the present state of development, these processes are clearly not competitive. The research for some of these methods is just getting started. It is entirely possible that some of these alternative processes will never be competitive for the large waste treatment plant that can afford the capitalization; the skilled operation and required manpower to operate a removal plant based, say, on lime precipitation and calcination. Special circumstances - perhaps the relatively small treatment plant - may dictate the selection of a process that has a higher unit cost for removing phosphates but which requires less attention.

I. Phosphorus Removal

Wastewaters may contain orthophosphate ($PO_4^{\equiv}$), condensed phosphates such as pyro or tripolyphosphate, or organic phosphorus compounds. Removals are affected by the form in which the phosphorus is present.

A. Sorption on Activated Alumina

Yee has published data showing the ability of activated alumina to sorb phosphates from water, Not only could phosphate be sorbed from solution by activated alumina but, most importantly, the sorbed phosphate can be quantitatively desorbed by appropriate regeneration chemicals.

Activated alumina is a synthetic material consisting largely of aluminum oxide which has been activated at high temperature. It is available in a variety of forms ranging from fine powders to granules. A particular property is its high specific surface area ranging from 200 - 400 square meters per gram. The probable mode of operation would be column contactors, much like those in current use for activated carbon.

General operating characteristics and breakthrough curves for orthophosphate (OP), hexametaphosphate (HTP), tripolyphosphate (TPP), and pyrophosphate (PP) are shown in Figures 1 and 2 respectively.

1. Advantages
    - a) Highly selective for phosphate
    - b) High removal efficiencies with low P residuals
    - c) No additional inorganic ions added
    - d) No pH change
    - e) Little effect from variations in feedwater composition or quality.
2. Chemical Costs
    - a) 3.9¢/1000 gal for feed containing 14 mg/1 P
    - b) 6.4¢/1000 gal for feed containing 23 mg/1 P

B. Exotic Precipitants - Lanthanum

In addition to the common precipitants, calcium, aluminum, and iron, lanthanum is known to produce a very insoluble salt with phosphate. Solubility products and calculated soluble phosphorus concentrations are shown in Figure 3.

In practice, however, these theoretical solubilities are not obtained with iron or aluminum even though large excesses of precipitants are added. The reasons apparently are that competing hydrolysis reactions reduce the concentration of metal ions available for phosphate precipitation. Non-hydrolyzing calcium added to wastewater in dosages several times greater than those of aluminum or iron reduces residual phosphate to about the same level although the theoretical solubility of hydroxyapatite, the form of the precipitate, is 6 - 7 orders of magnitude greater than solubility of the iron and aluminum phosphates. In short, solubility product is not an accurate guide to the practical usefulness of a precipitant. The extent of removal of phosphate by hydrolyzing metal ions like iron and aluminum really is a function of both solubility product, rate of reaction and importantly, of the competing hydrolysis reactions. Lanthanum which is only slightly hydrolyzed leaves a very low residual of phosphate over a broad pH range as shown in Figure 4.

A successful lanthanum precipitation process must meet the following criteria:

1) Phosphate should be readily reduced below 0.1 mg/l P despite varying concentrations of phosphate in influent wastewater.
2) Residual lanthanum in solution must be negligible.
3) Lanthanum in sludge must be almost completely recovered for reuse by an inexpensive process not yet investigated.

No cost data for a lanthanum precipitation process are available. Lanthanum oxide is about $3.00/lb, however, a lanthanum-rich mixture of rare earths is quoted at about 60¢/lb. This is obviously not competitive with alum at 3¢/lb, however, if recovery of lanthanum is complete, special circumstances may justify its use.

C. Ion Exchange

Ion exchange materials, both natural and synthetic, have potential for removing phosphates from wastewater, although their primary function is the removal of inorganic ions in general. Modifications can be made on natural ion-exchange materials to obtain a degree of selectivity for phosphate ion, in which case, ion exchange as a process for phosphate removal becomes more attractive.

A typical ion-exchange material can be looked upon as a microporous matrix containing many ionic sites, either all positive or all negative as shown in Figure 5. In order to maintain electro-neutrality, each fixed ionic site must have associated with it an ion of opposite charge called a counter ion. Depending on the counter ion the exchange material can be either a cation or anion exchanger. This counter ion must be mobile enough so that it can be replaced by, or exchanged for, another ion of the same charge upon contact with a solution of this new ion. When all of the original counter ion is replaced, the ion-exchange material is exhausted. A concentrated solution, 4 to 10 percent, of the original counter ion must be used to regenerate the ion exchanger.

Ion exchangers may be divided into two groups: (1) the natural ion-exchange materials such as the zeolites and clay minerals and (2) the synthetic organic resins. In alkaline wastewater, the dominant phosphate species is the $HPO_4^=$ and thus requires an anion exchanger for its removal. The naturally occurring ion exchangers have relatively low anion exchange capacities, however, research is underway on chemical modifications to increase their anion exchange capacities.

Synthetic anion exchangers have adequate capacities to remove anions from water but phosphate meets competition from other anions, particularly sulfate, for the available exchange sites. Typical breakthrough curves for various ions are shown in Figure 6.

In order for synthetic ion-exchange materials to become a competititve process, they must become highly selective for phosphate ion. Such selective resins have been developed for certain ions such as potassium, fluoride and borate. None, to my knowledge, has been developed for phosphate ion, and until such materials are made, synthetic ion exchangers will not be economically useful for removing phosphate.

D. Land Application

Soil systems as treatment devices, rather than as means of disposal, are receiving more attention as a potentially cheap method of treating wastes.

Soil is a composite medium that may contain relatively inert rock, gravel and sand as well as reactive clays and minerals; and additionally, varying amounts of organic materials such as humus, living and dead vegetable and animal matter. Many of the components possess useful properties to accomplish effective waste treatment. Treatment mechanisms include biological oxidation, chemical precipitation, ion exchange, adsorption, chemical oxidation and plant assimilation. The sum total of these effects is capable of providing very effective treatment of wastewater.

Phosphate removals by 6 feet of soil in field and lysimeter studies at Westby, Wisconsin, and Loveland, Ohio, are shown in Figure 7. Other data show that approximately 75% of the phosphate is removed in the upper 1-foot layer of soil. As shown in Figure 8, these systems had not begun to exhaust the potential for phosphate removal.

One disadvantage of a soil disposal system is that large land areas are required to handle large flows. The Westby and Loveland systems were operated at about 1 gallon per day/sq.ft. Hydraulic failure is likely to occur before the phosphate removal capacity is reached.

E. Reverse Osmosis

When two solutions of unequal salt concentration are separated by a semi-permeable membrane, there is a tendency for pure water to flow from the more dilute to the more concentrated solution. The driving force that impels this flow through the membrane is related to the osmotic pressure of the system, and this pressure is proportional to the difference in concentration between the two solutions. The principle is illustrated in Figure 9A. If the liquid on the more concentrated side is allowed to rise in a standpipe as water passes through the membrane, as shown in Figure 9B, the hydrostatic pressure on the right side of the membrane gradually increases until it finally equals the osmotic pressure. At this point, flow through the membrane ceases. If, then, we intentionally increase the pressure on the more concentrated (right) side of the membrane, as shown in Figure 9C, the flow of water through the membrane reverses, that is, water moves from the more concentrated compartment. This method of purifying water is popularly called reverse osmosis, though the mechanism of water transfer may not be the same as in normal osmosis.

Membranes can be made with selectivity for certain ionic or nonionic materials, but current research is directed toward development of membranes which remove all contaminating substances. However, as a general rule, ion removal is directly proportional to ion valence, thus multivalent phosphate and sulfate are more readily removed than monovalent chloride.

Large scale tests of reverse osmosis have shown that virtually 100% of the phosphate ion is removed by "tight" membranes while 94% is removed by the "looser" membranes. A reverse osmosis unit currently available from a manufacturer has been designed to remove organic and particulate matter and to operate at the relatively low pressure of less than 100 pounds per square inch. Ninety-five percent removal of the phosphate ion is claimed. The manufacturer puts the cost of the total treatment, which includes phosphate removal, at about 30¢/1000 gallons.

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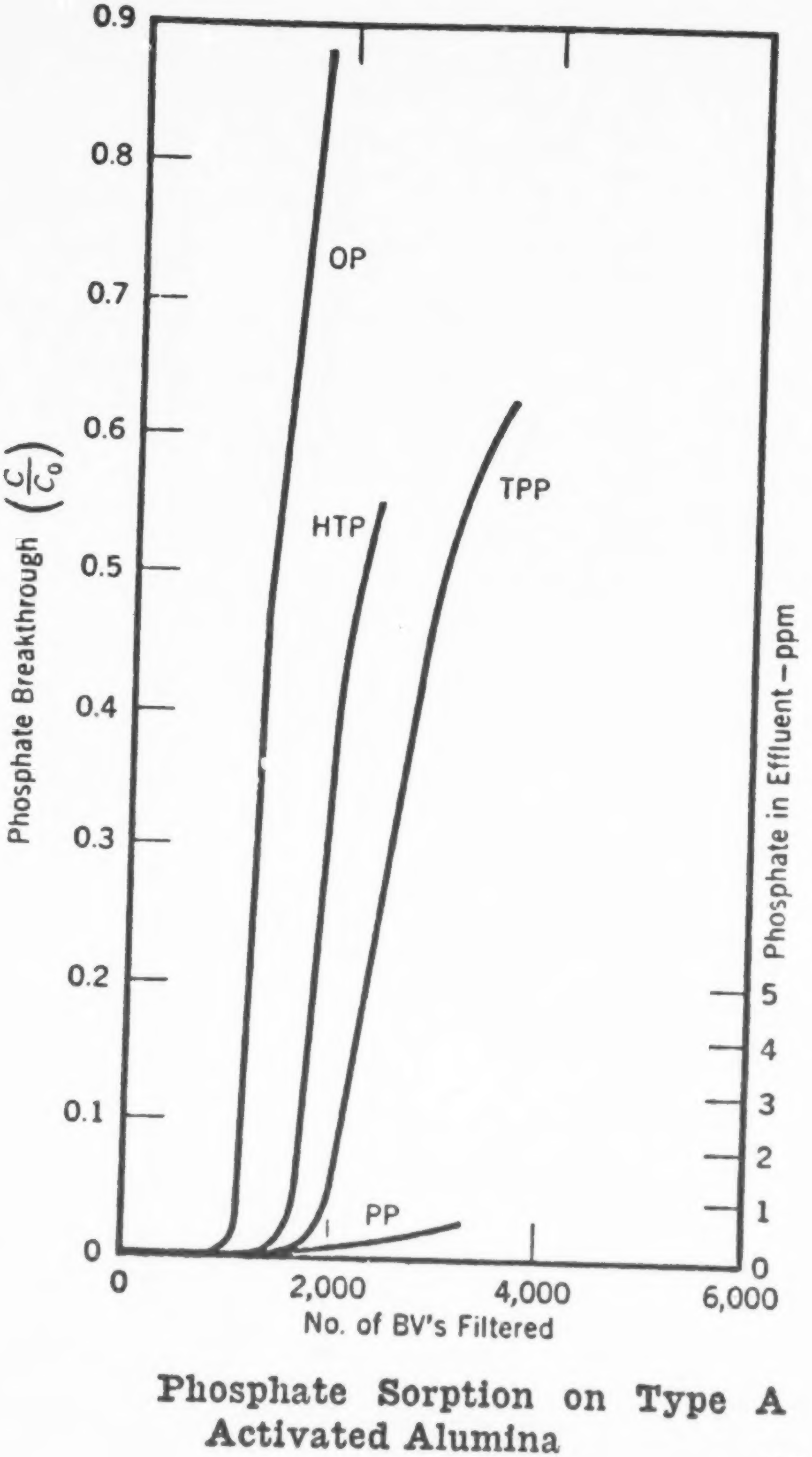
*Evaluation of Three Commercial Aluminas**

Item	Type of Alumina		
	A	B	C
Cost—*¢/lb*	12	100	40
Surface area—*sq m/g*	250	250	400
Alumina sorption capacity for mixed phosphates (as PO_4^{3-})—*mg/g*	19	17	>27
Mixed phosphates (as PO_4^{3-}) eluted from alumina in regeneration—*mg/g*	17	10	28
Regenerant waste—*BV's*	12	16	12
Alumina dissolved in regeneration—*per cent*	8	5	35

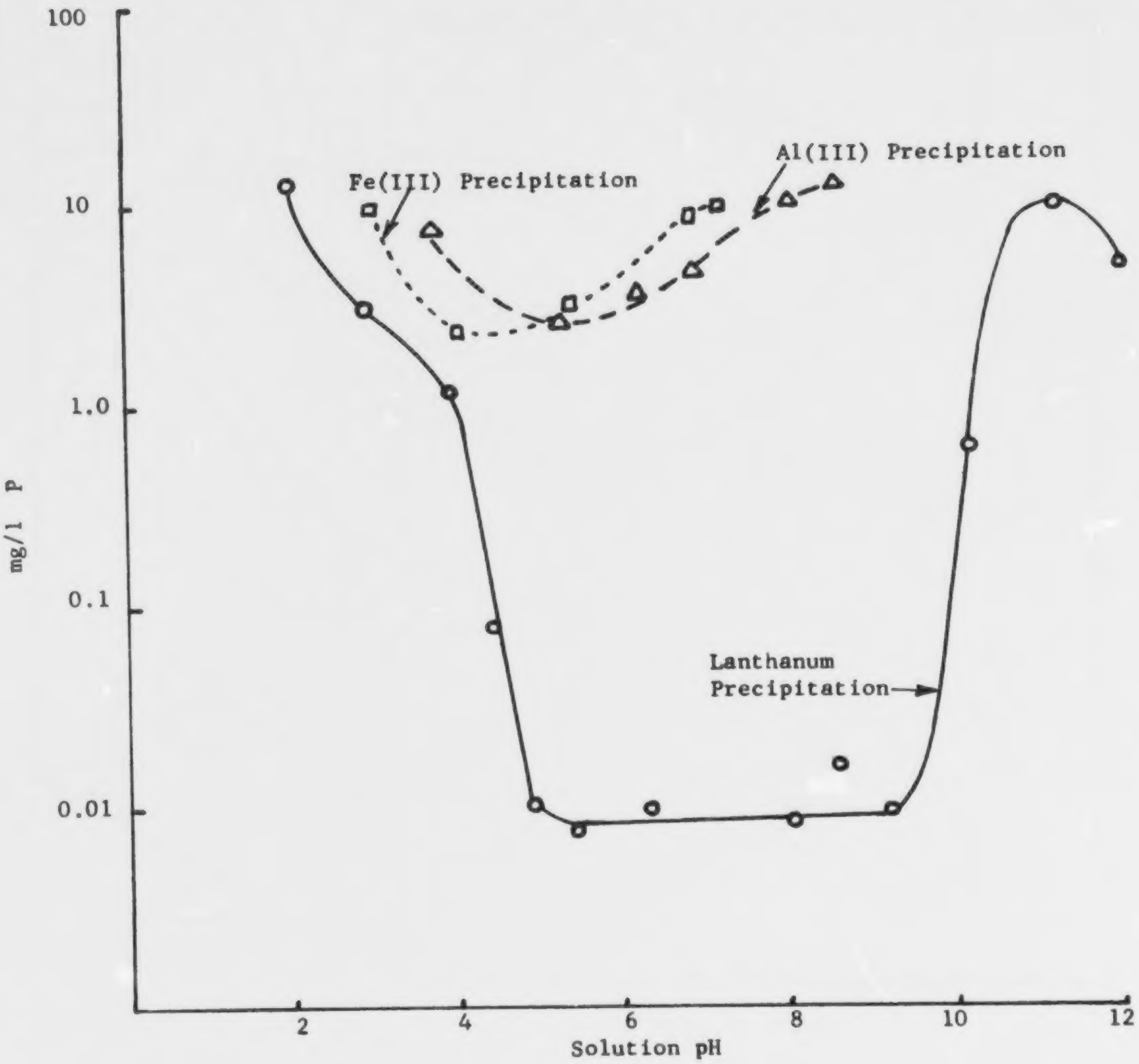
* Performances were evaluated in upflow through fluidized beds.



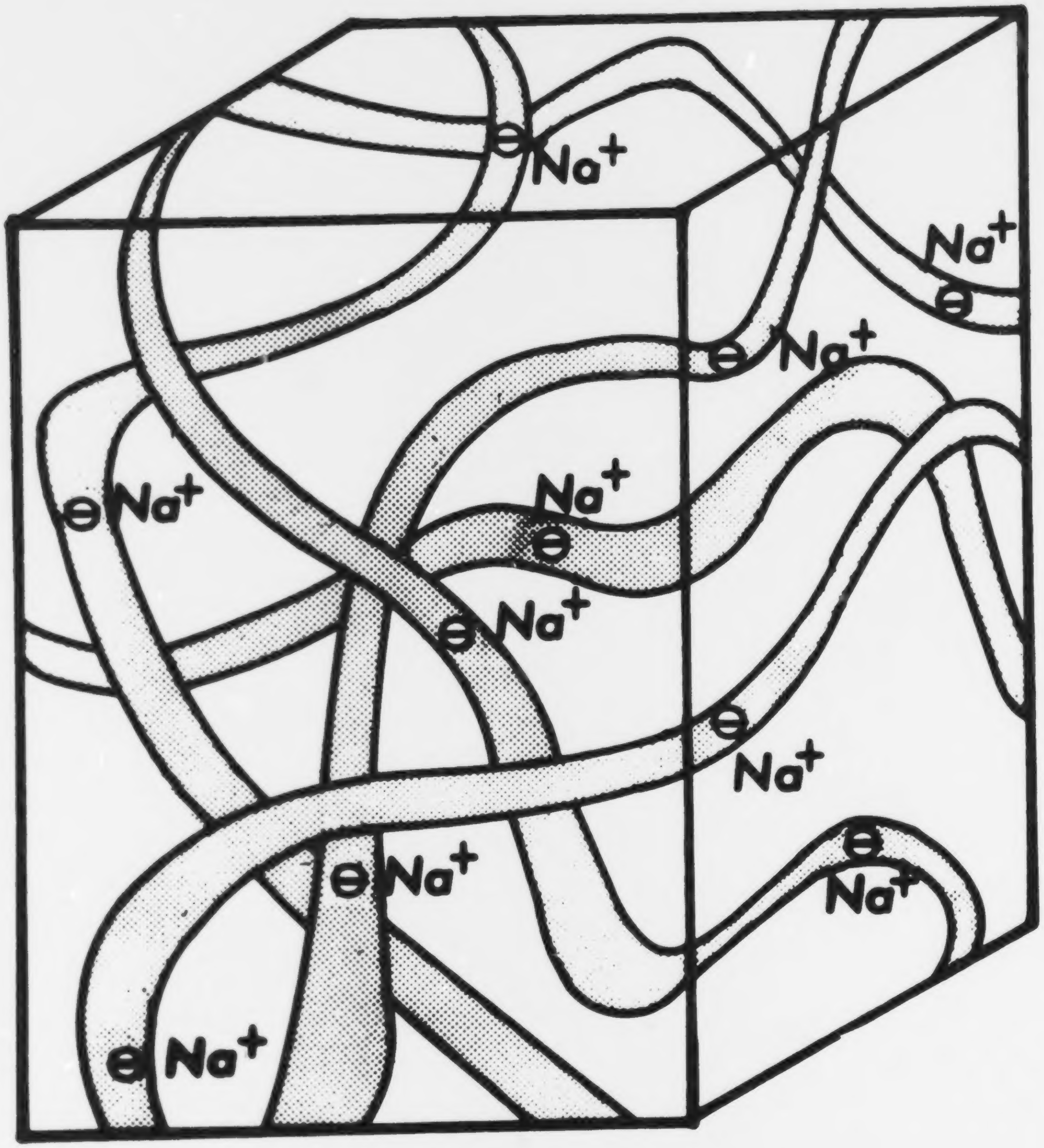
Phosphate Sorption on Type A Activated Alumina

SOLUBILITY OF PHOSPHATES

SALT	K_{SP}	CALCULATED SOLUBLE P MG/L
$FE\ PO_4$	10^{-23}	9×10^{-8}
$LA\ PO_4$	3.75×10^{-23}	2×10^{-7}
$AL\ PO_4$	10^{-21}	9×10^{-7}
$(MG)_3(PO_4)_2$	2×10^{-27}	0.1
$CA_{10}(OH)_2(PO_4)_6$	10^{-90}	0.3



Precipitation of Orthophosphate at 1:1 Metal-to-Phosphate Stoichiometry
Phosphate Solution used: 12 mg/l P Na_2HPO_4


⊖ Na+
⊖ Na+
⊖ Na+
⊖ Na+
⊖ Na+
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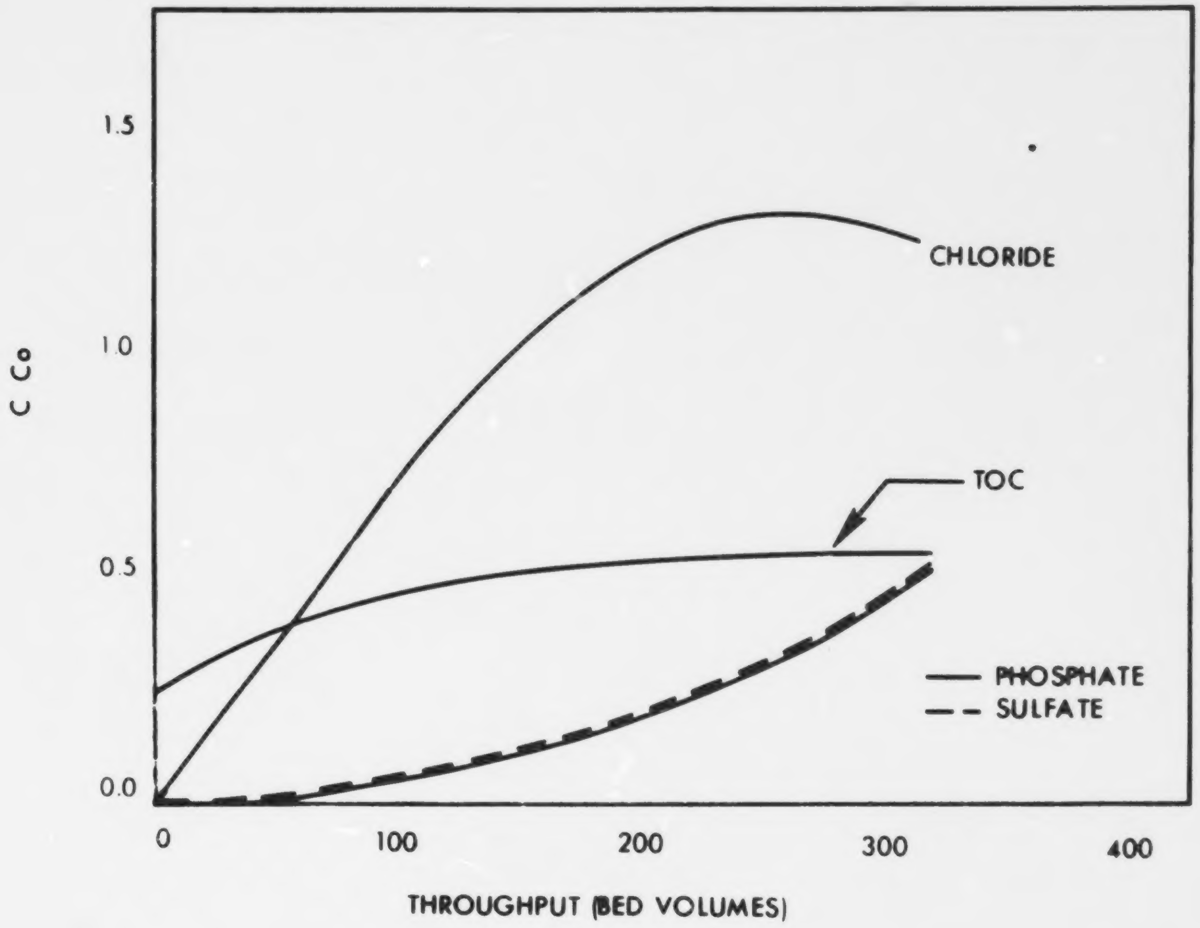
⊖ Na+
⊖ Na+
⊖ Na+
⊖ Na+
⊖ Na+

TYPICAL EXCHANGE MATERAL



BREAKTHROUGH PATTERNS FOR ANION EXCHANGE

EXPERIMENTAL RESULTS

PHOSPHATE REMOVAL IN SILT LOAM

	INFLUENT P MG/L	6 FT PERCOLATE MG/L	PERCENT REMOVAL
WESTBY			
SOIL & VEGETATION	9.7	2.4	75(1)
SOIL & VEGETATION	9.7	0.7	93
LOVELAND			
BARE SOIL, WINTER	6.3	0.3	95
BARE SOIL, SUMMER	11.5	0.2	98
SOIL & VEGETATION, SUMMER	11.5	0.15	99
BARE SOIL, ANAEROBIC	13	1.0	92

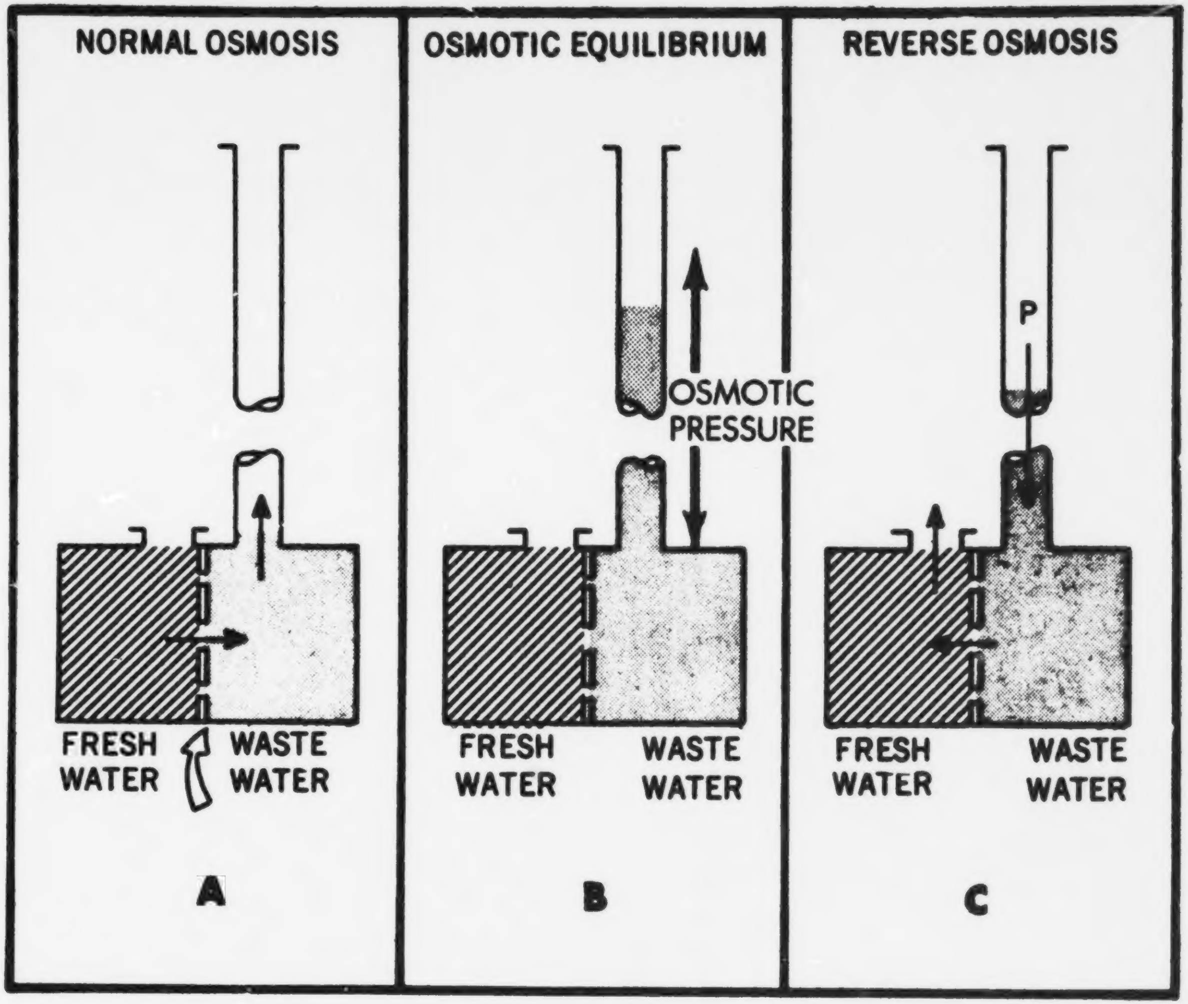
(1) 1 FT PERCOLATE

EXPERIMENTAL RESULTS

PHOSPHATE REMOVAL

		DURATION	PHOSPHATE-P REMOVAL (1)
WESTBY SYSTEM (SILT LOAM)		6 YEARS	1.6
LOVELAND SYSTEM (SILT LOAM)		1.5 YEARS	0.4
			CAPACITIES (2)
SASSAFRAS SOIL	p^H 6.5		11.2
COLLINGTON SOIL	p^H 6.5		40
DUTCHESS SOIL	p^H 6.5		35

(1) TONS PER ACRE-HALF-FOOT
(2) BAILEY, FROM TOTH & BEAR, 1947 - THESE ARE SANDY SOILS.


NORMAL OSMOSIS
OSMOTIC EQUILIBRIUM
REVERSE OSMOSIS
OSMOTIC PRESSURE
P
FRESH WATER
WASTE WATER
FRESH WATER
WASTE WATER
FRESH WATER
WASTE WATER
A
B
C

Schematic representation of principles involved in normal osmosis and reverse osmosis.

COMBINED TREATMENT FOR REMOVAL OF PHOSPHORUS AND NITROGEN

Edwin F. Barth

I. Importance of Nitrogen from a Treatment and Control Standpoint

   A. Ammonia exerts oxygen demand in receiving water

   B. Various forms of nitrogen effect chlorination practice

   C. Oxidized nitrogen can be a health hazard

   D. Nitrogen compounds are algae nutrients

II. Nitrogen Removal in Conventionally Designed Treatment Plants

   A. Field survey

      1. Nitrogen removal has no correlation with solids or organic removal

      2. Mass balance of nitrogen in municipal plants

      3. Biological reactions must be basis for design

III. Cycle of Nitrogen During Biological Treatment

   A. Transformations in a batch system

   B. Pathways in a continuous system

      1. Control of nitrification depends on sludge wasting schedule

IV. Development of a Three Sludge System to Control Biological Denitrification

   A. Initial process modifications

      1. Long detention times and poor process control encountered

B. Three sludge system isolates unit processes and allows control of biological reactions
  1. Methanol addition forces denitrification

V. Combination of Mineral Addition with Three Sludge System Denitrification Allows Control of Both Nitrogen and Phosphorus
  A. Chemical and biological reactions are compatible
  B. Each unit process has specific function
    1. High-rate activated sludge is site of carbon oxidation and cellular synthesis. Sodium aluminate precipitates phosphorus.
    2. Nitrification unit has low sludge synthesis and assures complete nitrification
    3. Denitrification unit has high efficiency because a synthetic organic chemical is used
      a. Methanol is oxidized rather than synthesized into new cells
      b. Very cheap organic carbon source
  C. Mass balances of nitrogen and phosphorus show function of each unit operation
  D. Mixed liquor characteristics are enhanced by aluminum addition
    1. Improved sludge-density index
    2. Higher mixed liquor solids possible in high-rate activated sludge

102<

E. Aluminum phosphate does not dissolve during anaerobic digestion of waste activated sludge
    1. Sludges show high phosphorus and aluminum content

VI. Cost of Combined Treatment for Removal of Nitrogen and Phosphorus
    A. Capital
    B. Operating

VII. Grant and Contract Work in Area of Combined Treatment for Nitrogen and Phosphorus
    A. University of Notre Dame, 50,000 gpd
    B. Manassas, Virginia, 0.2 mgd

VIII. Other Biological Denitrification Studies
    A. Packed pressure columns
        1. Pomona, California, 7 gallons per minute per square foot
            a. Granular carbon treating secondary effluent
            b. Methanol injected to force denitrification
    B. Large media flooded columns
        1. Firebaugh, California, 2 gallons per minute per square foot
            a. Stone type media
            b. Methanol added to force denitrification
        2. Aerojet-General
            a. Bench scale study of endogenous source of organic carbon

- C. Deep pond denitrification
  - 1. Firebaugh, California, 4-day detention time
    - a. Low concentration of active organisms
    - b. Methanol added to force denitrification

IX. Other Approaches to Nitrogen Removal

- A. Chemical approaches are limited because most nitrogen compounds in wastewater are soluble
  - 1. pH adjustment and air stripping of ammonia
    - a. Temperature effect process efficiency
  - 2. Formation of magnesium ammonium phosphate
    - a. Limited in application
  - 3. Advanced processes such as reverse osmosis, ion exchange
    - a. Not specific for nitrogen compounds
    - b. High capital cost

IMPORTANCE OF NITROGEN

NH_3 in effluents can cause DO sag in receiving water

NH_3 is corrosive to copper fittings

1 NH_3 requires 7 plus Cl_2 for breakpoint

NO_2 causes high Cl_2 demand

NH_3 influences Cl_2 contact time

Nitrogen compounds are nutrients

NO_3 can be health hazard

RELATIONSHIP OF CARBON OXIDATION AND NITROGEN OXIDATION

	mg/l	
	Wastewater	Final Effluent
Organic Matter	250	25
Organic Oxygen Demand	375	37
NH_3	25	20
Ammonia Oxygen Demand	112	90
Total Oxygen Demand	487	127
Oxygen Demand Due to NH_3	22%	71%

UNIT EFFICIENCIES, PER CENT REMOVAL

Plant	Primary			Secondary			Overall		
	COD	SS	N	COD	SS	N	COD	SS	N
Archbold	43	58	9	89	87	57	94	94	61
Hamilton	55	57	-27	77	86	34	90	94	16
Lebanon	62	65	28	45	55	42	79	84	58
Loveland	0	15	0	61	56	30	61	62	30
Milford	23	55	17	60	61	25	69	82	38

MIXED LIQUOR CHARACTERISTICS AFTER ADDITION OF ALUMINUM

	Sludge Age days (Approx.)	MLSS mg/1	MLVSS mg/1	% Volatile	SDI	% Nitrogen V. S. Basis	% Phosphorus V. S. Basis	% Aluminum V. S. Basis
High-Rate Mixed Liquor	2	3,385	1,740	51	1.12	8.3	12.3	11.0
Nitrification Mixed Liquor	22	1,195	770	64	1.15	10.6	8.0	6.6
Denitrification Mixed Liquor	38	2,010	1,385	69	1.46	9.7	8.7	6.0

EFFECT OF ALUMINUM ON SLUDGES AND SUPERNATANT

1. HIGH-RATE MIXED LIQUOR CHARACTERISTICS

	MLSS mg/1	MLVSS mg/1	% VOLATILE	SDI	ORGANIC LOAD lb COD/day/ lb MLVSS
BEFORE Al^{+++}	1,450	900	62	0.44	2.6
AFTER Al^{+++}	3,385	1,740	51	1.12	1.6

2. PERCENT PHOSPHORUS IN SLUDGES - TOTAL SOLIDS BASIS

	PRIMARY	WASTE ACTIVATED	MIXED PRIMARY PLUS W. ACTIVATED	DIGESTED
BEFORE Al^{+++}	1.1	2.1	1.6	2.2
AFTER Al^{+++}	1.1	6.2	4.5	5.2

3. TOTAL PHOSPHORUS IN SUPERNATANT - mg/1

BEFORE Al^{+++}	170
AFTER Al^{+++}	60

CHANGE IN COMPOSITION OF PROCESS STREAM DURING TREATMENT

PROCESS STREAM	mg/1							
	COD	S. S.	TOTAL P	ORG. N	NH_3 N	NO_2 N	NO_3 N	TOTAL N
RAW WASTEWATER	320	157	12.6	10.3 +	11.3 +	/	/ =	21.6
PRIMARY EFFLUENT	218	90	11.9	5.9 +	13.7 +	/	/ =	19.6
HIGH-RATE EFFLUENT	64	9	2.8	0.8 +	7.7 +	1.1 +	4.3 =	13.9
NITRIFIED EFFLUENT	43	7	2.6	0.4 +	0.6 +	0.3 +	11.5 =	12.8
FINAL (DENITRIFIED) EFFLUENT	44	7	1.5	0.4 +	0.3 +	0.3 +	0.9 =	1.9
PERCENT (%) REMOVAL	86	95	88					91

COMPARISON OF TWO COLUMN DENITRIFICATION OPERATIONS

		POMONA	FIREBAUGH
1.	FEED WATER	SECONDARY EFFLUENT	AGRICULTURAL DRAINAGE
2.	MEDIA	SAND, CARBON	GRAVEL, CINDERS
3.	MEAN PARTICLE DIAMETER	CARBON - 0.877 mm SAND - 0.965 mm	1/2" to 1"
4.	COLUMN DIA.	2" and 6'	4" and 18"
5.	COLUMN HT.	10'	6'
6.	FLOW DIRECTION	DOWNFLOW	UPFLOW
7.	SURFACE LOADING RATE	7 gpm/ft^2	0.4 gpm/ft^2
8.	CLIMATE	SOUTHERN CALIFORNIA	NORTHERN CALIFORNIA
9.	NO$_3$ LEVEL	15 to 20 mg/l as N	20 mg/l as N
10.	EMPTY BED CONTACT TIME	LESS THAN 10 MIN.	1 to 2 HOURS
11.	DENITRIFICATION EFFICIENCY	90% +	90% +
12.	BACKWASH REQUIREMENTS	DAILY FOR 45 - 60 MIN.	NONE
13.	CH$_3$OH UTILIZATION RATE	1.8/1 @ DO = 0.6 2.4/1 @ DO = 5.4	2.7/1

PARAMETERS AFFECTING
COLUMN DENITRIFICATION

	PARAMETER		FACTORS AFFECTED
1.	MEDIA SIZE	-	SURFACE AREA, DIFFUSION DISTANCE
2.	MEDIA PACKING ARRANGEMENT	-	POROSITY
3.	MEDIA GRADATION	-	POROSITY
4.	COMBINATION OF MEDIA SIZE, PACKING ARRANGEMENT, AND GRADATION	-	FRICTION LOSS, FREQUENCY OF BACKWASHING, CONCENTRATION OF ORGANISMS
5.	BACKWASHING	-	SLIME THICKNESS
6.	SLIME THICKNESS	-	FRICTION LOSS, CONCENTRATION OF ORGANISMS
7.	DISSOLVED OXYGEN	-	METHANOL DOSE
8.	METHANOL DOSE	-	COMPLETENESS OF REACTION
9.	TEMPERATURE	-	RATE OF BIOLOGICAL ACTIVITY
10.	DIRECTION OF FLOW	-	SURFACE LOADING RATE
11.	SURFACE LOADING RATE	-	FRICTION LOSS

CAPITAL EQUIPMENT REQUIREMENTS
FOR NUTRIENT REMOVAL

MINERAL ADDITION

1. DUAL OPEN LOOP CONTROL SYSTEM
2. CHEMICAL STORAGE AND DOSING TANKS

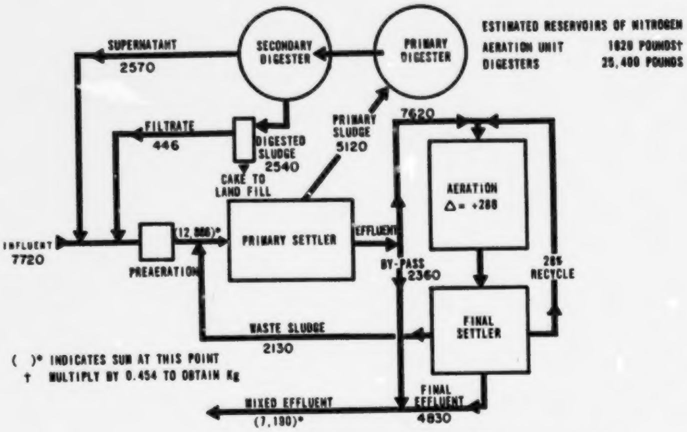
OPEN TANK DENITRIFICATION

1. DUAL OPEN LOOP CONTROL SYSTEM
2. CHEMICAL STORAGE AND DOSING TANKS
3. 33% ADDITIONAL MIXED LIQUOR TANKAGE WITH PROVISIONS FOR SLOW AGITATION
4. 2 ADDITIONAL SECONDARY CLARIFIERS
5. 2 ADDITIONAL SLUDGE RETURN SYSTEMS

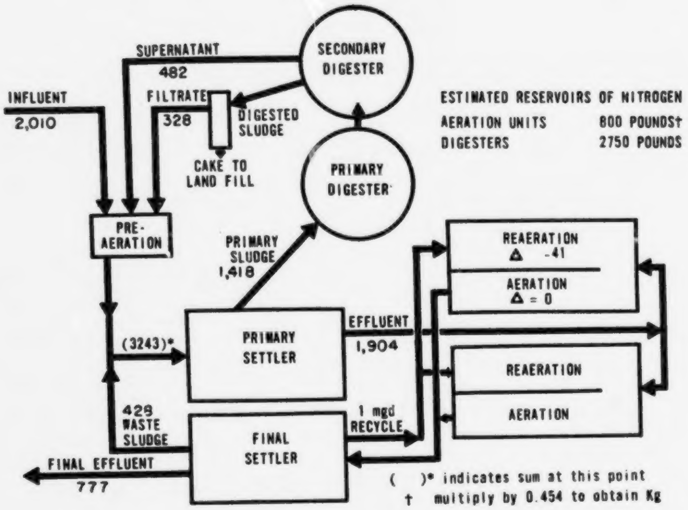
COLUMN DENITRIFICATION

1. DUAL OPEN LOOP CONTROL SYSTEM
2. CHEMICAL STORAGE AND DOSING TANKS
3. 1 ADDITIONAL SECONDARY CLARIFIER
4. 1 ADDITIONAL SLUDGE RETURN SYSTEM
5. COLUMN SYSTEM
6. BACKWASH PUMP AND STORAGE TANK

5. COLUMN SYSTEM
6. RAPID SAND FILTER SYSTEM
7. BACKWASH PUMP AND STORAGE TANK

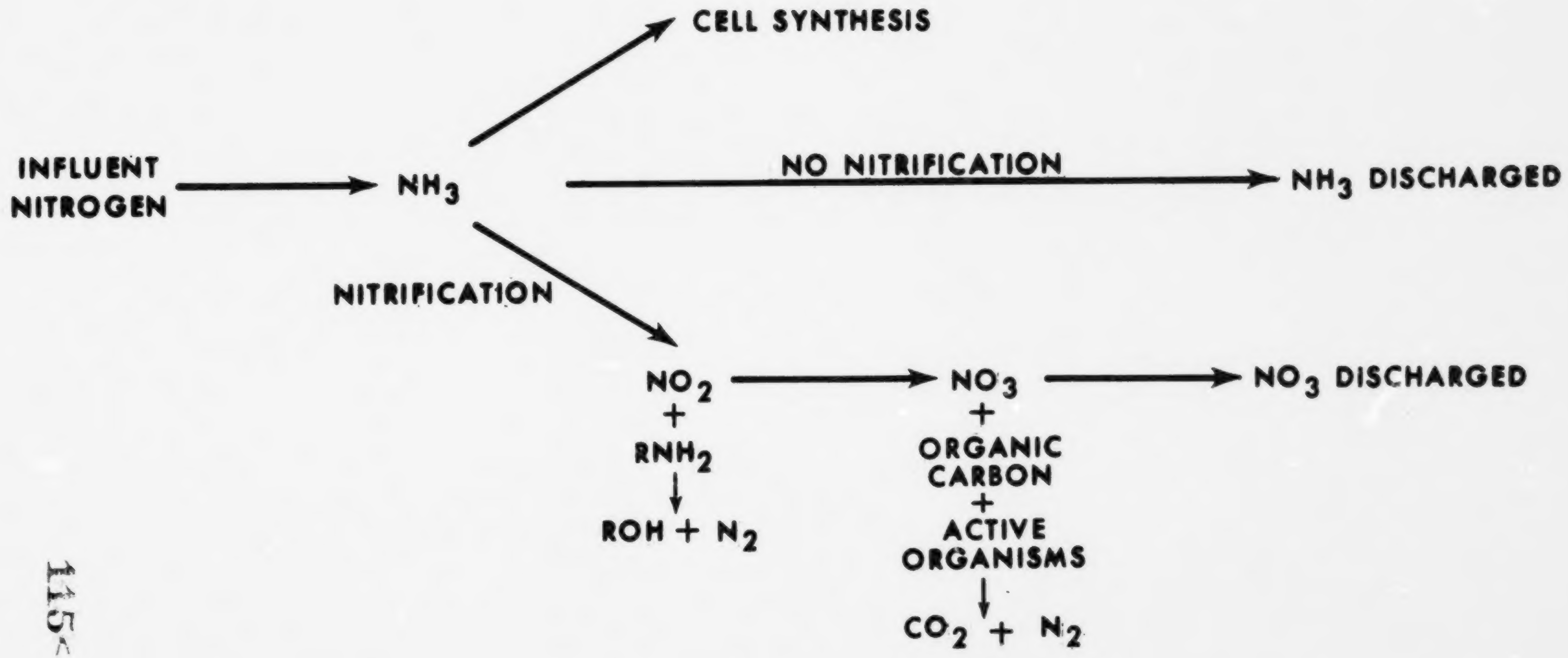

SUPERNATANT
2570
SECONDARY DIGESTER
PRIMARY DIGESTER
ESTIMATED RESERVOIRS OF NITROGEN
AERATION UNIT 1020 POUNDS†
DIGESTERS 25,400 POUNDS
FILTRATE
446
DIGESTED SLUDGE
2540
CAKE TO LAND FILL
PRIMARY SLUDGE
5120
7620
AERATION
Δ = +288
INFLUENT
7720
PREAERATION
(12,866)*
PRIMARY SETTLER
EFFLUENT
BY-PASS
2360
28% RECYCLE
WASTE SLUDGE
2130
FINAL SETTLER
( )* INDICATES SUM AT THIS POINT
† MULTIPLY BY 0.454 TO OBTAIN Kg
MIXED EFFLUENT
(7,190)*
FINAL EFFLUENT
4830

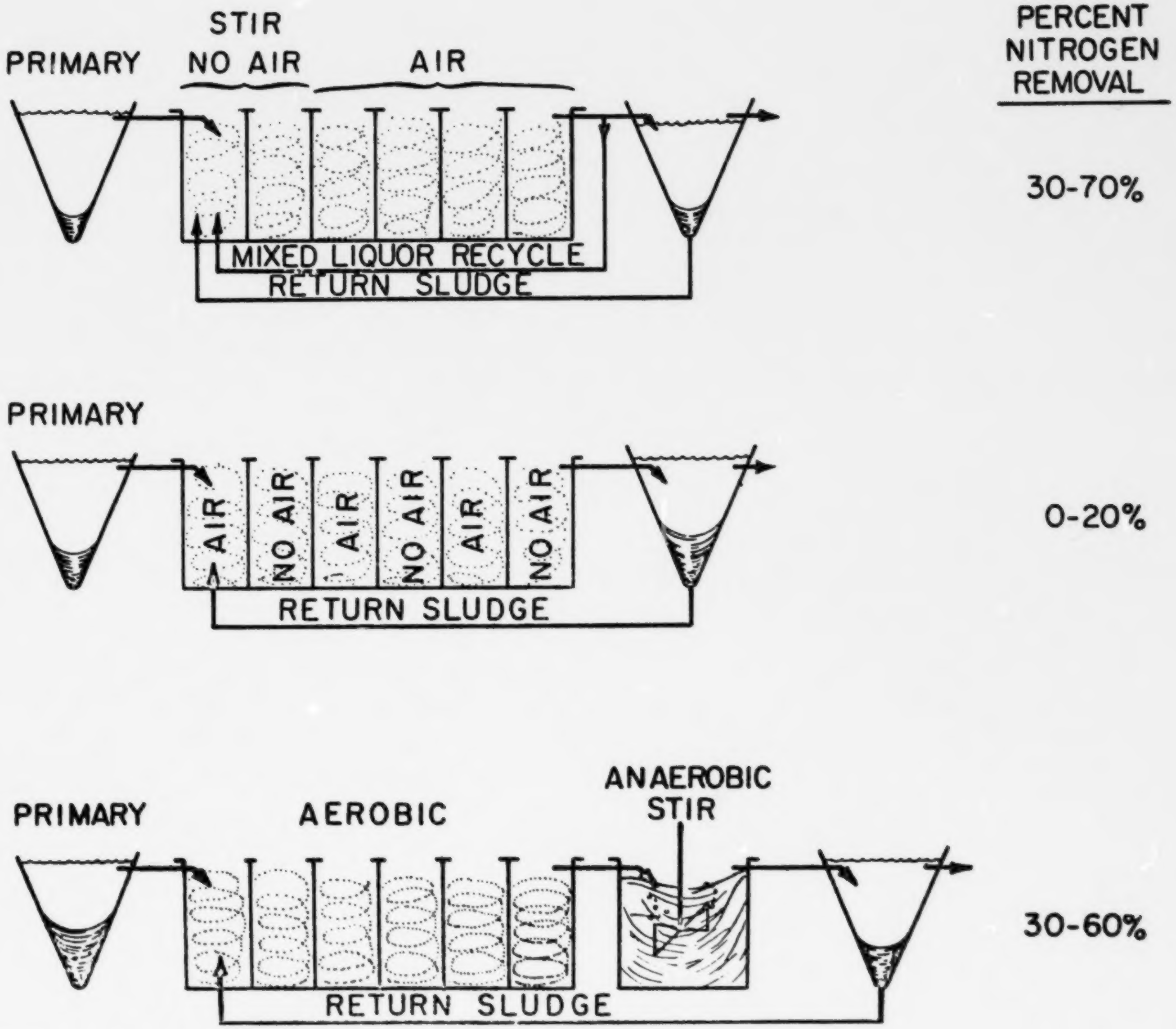
Five-day nitrogen balance, Hamilton, Ohio.
All values expressed in lb.


SUPERNATANT
482
SECONDARY DIGESTER
INFLUENT
2,010
FILTRATE
328
DIGESTED SLUDGE
CAKE TO LAND FILL
ESTIMATED RESERVOIRS OF NITROGEN
AERATION UNITS 800 POUNDS†
DIGESTERS 2750 POUNDS
PRIMARY DIGESTER
PRE-AERATION
PRIMARY SLUDGE
1,418
REAERATION
Δ -41
AERATION
Δ = 0
(3243)*
PRIMARY SETTLER
EFFLUENT
1,904
REAERATION
AERATION
423
WASTE SLUDGE
FINAL SETTLER
1 mgd
RECYCLE
FINAL EFFLUENT
777
( )* indicates sum at this point
† multiply by 0.454 to obtain Kg

Five-day nitrogen balance, Archbold, Ohio.
All values expressed in lb.

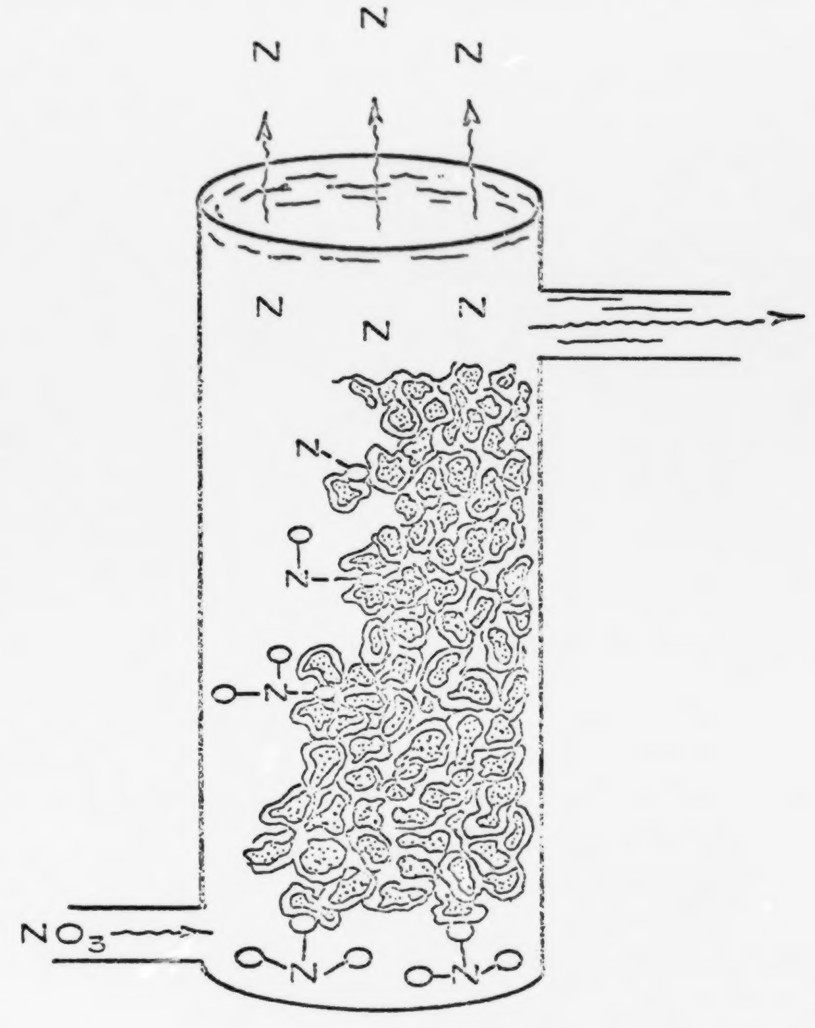
NITROGEN CYCLE


INFLUENT NITROGEN
NH_3
CELL SYNTHESIS
NO NITRIFICATION
NH_3 DISCHARGED
NITRIFICATION
$NO_2 + RNH_2 \rightarrow ROH + N_2$
NO_3 + ORGANIC CARBON + ACTIVE ORGANISMS $\rightarrow CO_2 + N_2$
NO_3 DISCHARGED

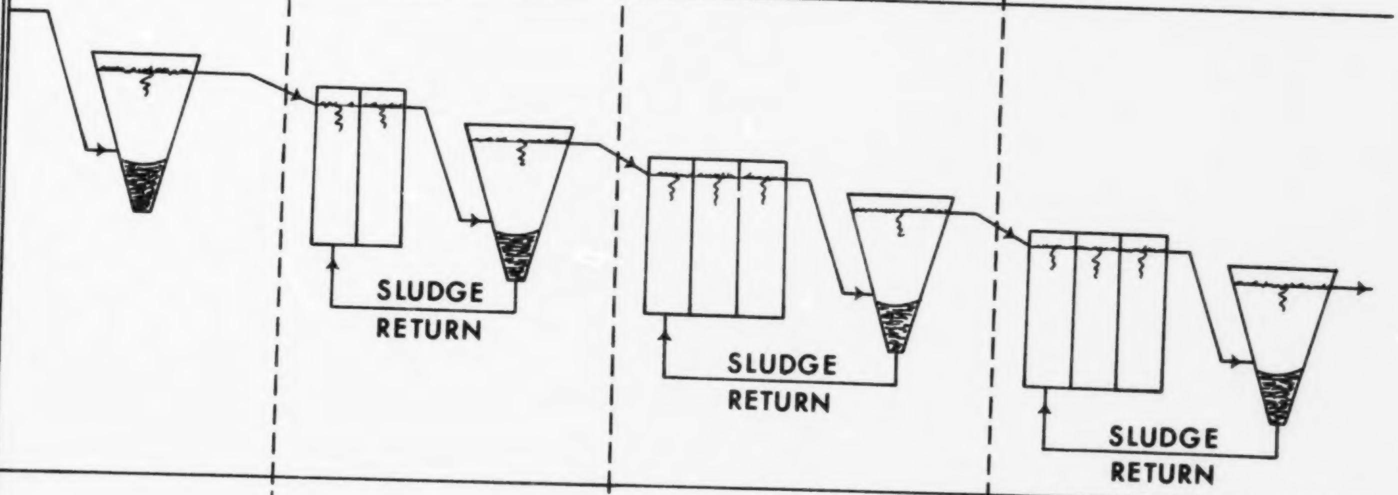

PRIMARY
STIR
NO AIR
AIR
MIXED LIQUOR RECYCLE
RETURN SLUDGE
PERCENT NITROGEN REMOVAL
30-70%
PRIMARY
AIR
NO AIR
AIR
NO AIR
AIR
NO AIR
RETURN SLUDGE
0-20%
PRIMARY
AEROBIC
ANAEROBIC STIR
RETURN SLUDGE
30-60%

REMOVAL OF NITROGEN BY BACTERIAL ACTION-FILTER METHOD

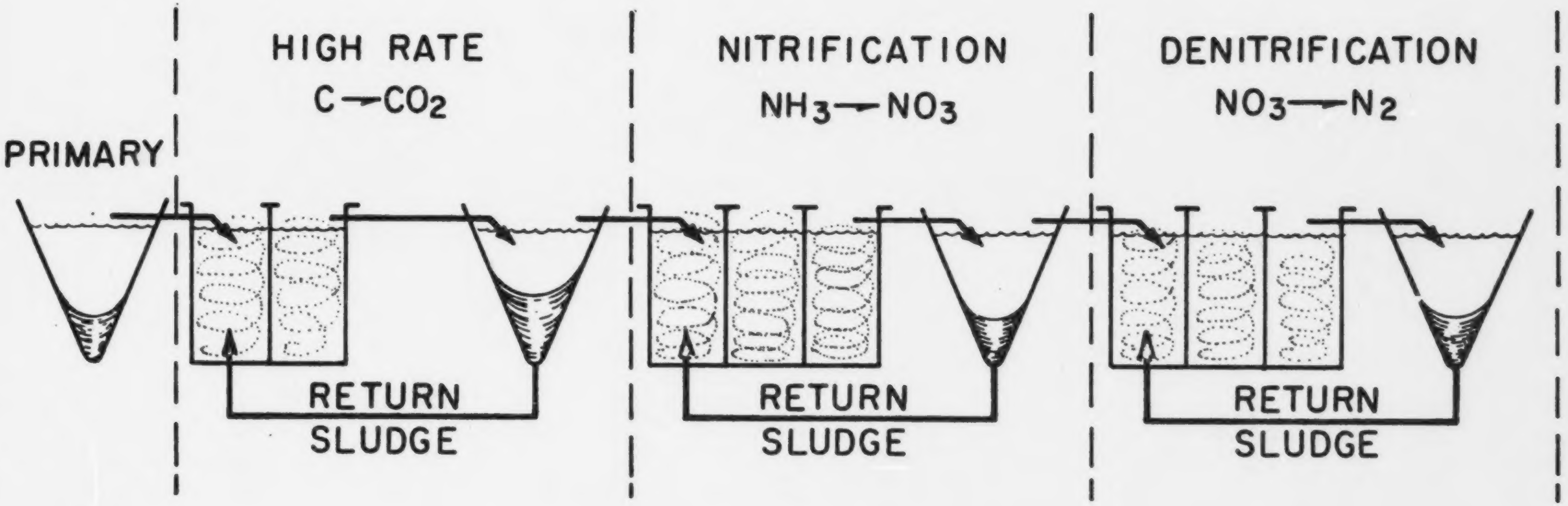
AGRICULTURAL WASTE WATER TREATMENT CENTER


N
N
N
N
N
N
N
O-N-O
O
O-N-O
O-N-O
O-N-O
NO_3

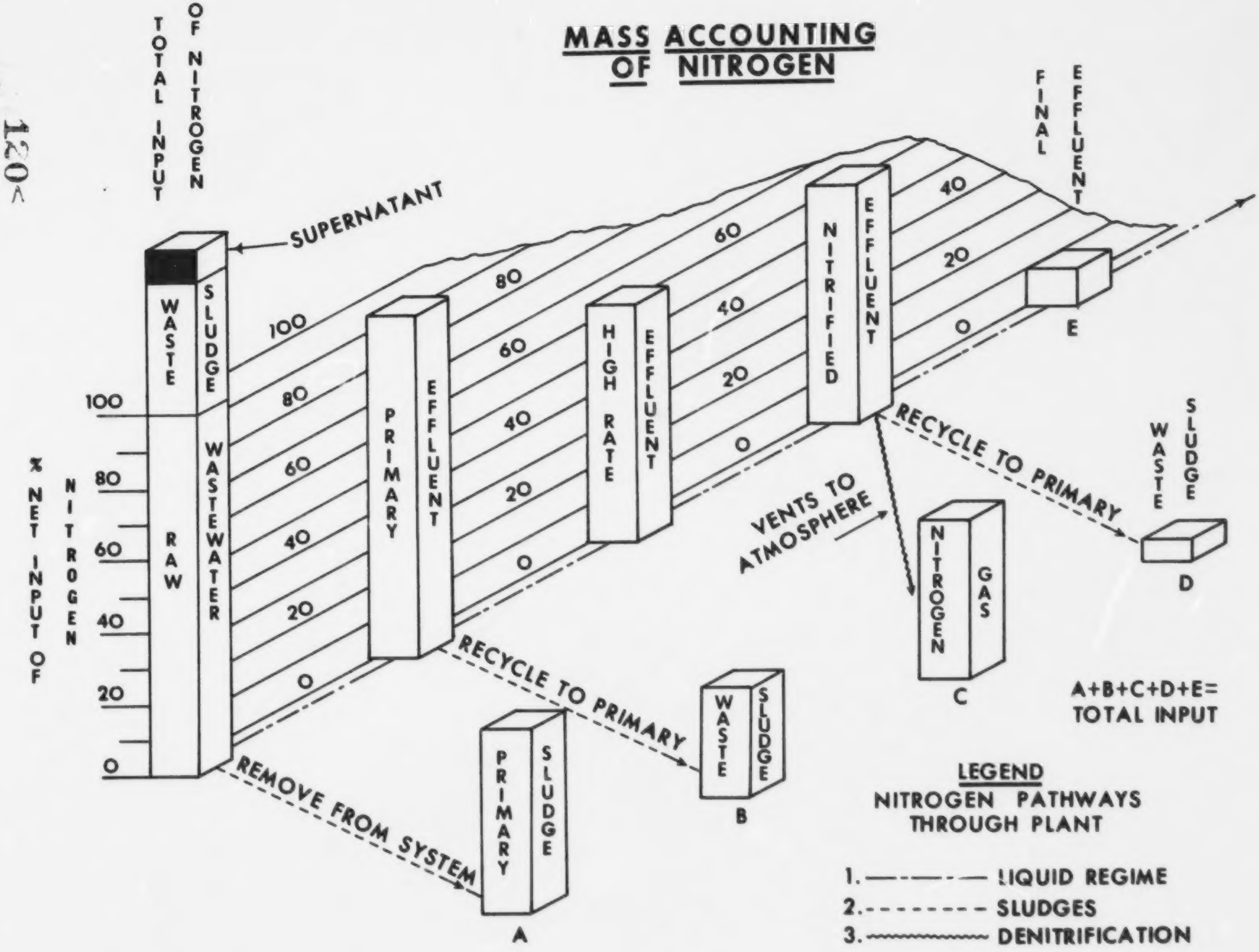
MAJOR PROCESS FUNCTIONS	REMOVE SETTLEABLE SOLIDS AND PARTICULATE COD	REMOVE BULK OF SOLUBLE ORGANICS AND PRECIPITATE PHOSPHORUS	CONVERT NH_3 TO NO_3	CONVERT NO_3 TO NITROGEN GAS AND CO_2 AND FURTHER REDUCE PHOSPHORUS
CHEMICAL ADDITIVES	NONE	SODIUM ALUMINATE	NONE	SODIUM ALUMINATE AND METHYL ALCOHOL
Unit	Primary	High–Rate	Nitrification	Denitrification


SLUDGE RETURN
SLUDGE RETURN
SLUDGE RETURN

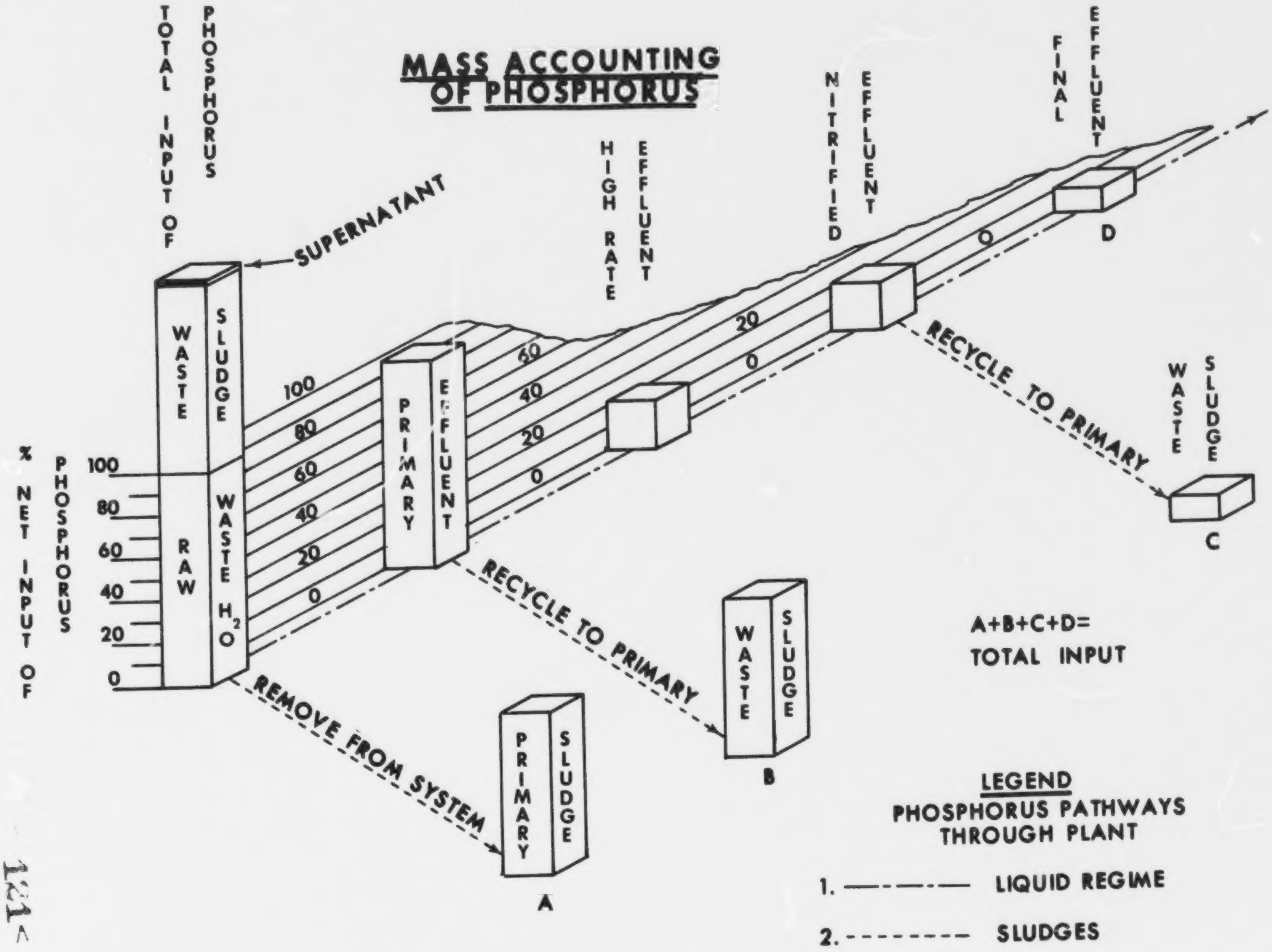
PROCESS FLOW DIAGRAM


PRIMARY
HIGH RATE
C → CO_2
NITRIFICATION
NH_3 → NO_3
DENITRIFICATION
NO_3 → N_2
RETURN SLUDGE
RETURN SLUDGE
RETURN SLUDGE

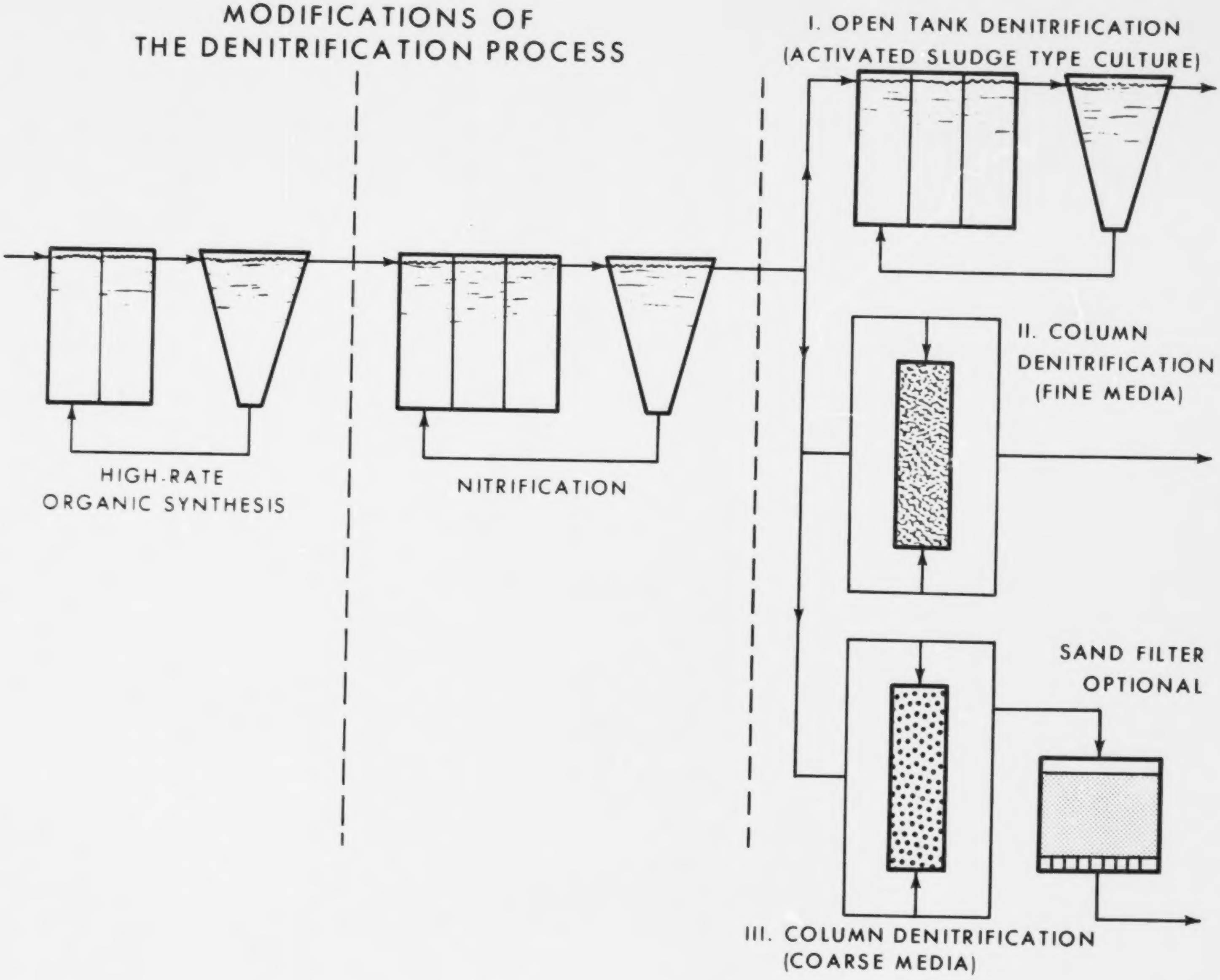
MASS ACCOUNTING OF NITROGEN


TOTAL INPUT OF NITROGEN
SUPERNATANT
WASTE SLUDGE
RAW WASTEWATER
% NET INPUT OF NITROGEN
100
80
60
40
20
0
PRIMARY EFFLUENT
HIGH RATE EFFLUENT
NITRIFIED EFFLUENT
FINAL EFFLUENT
REMOVE FROM SYSTEM
RECYCLE TO PRIMARY
RECYCLE TO PRIMARY
VENTS TO ATMOSPHERE
PRIMARY SLUDGE
A
WASTE SLUDGE
B
NITROGEN GAS
C
WASTE SLUDGE
D
E
A+B+C+D+E= TOTAL INPUT
LEGEND
NITROGEN PATHWAYS THROUGH PLANT
1. LIQUID REGIME
2. SLUDGES
3. DENITRIFICATION

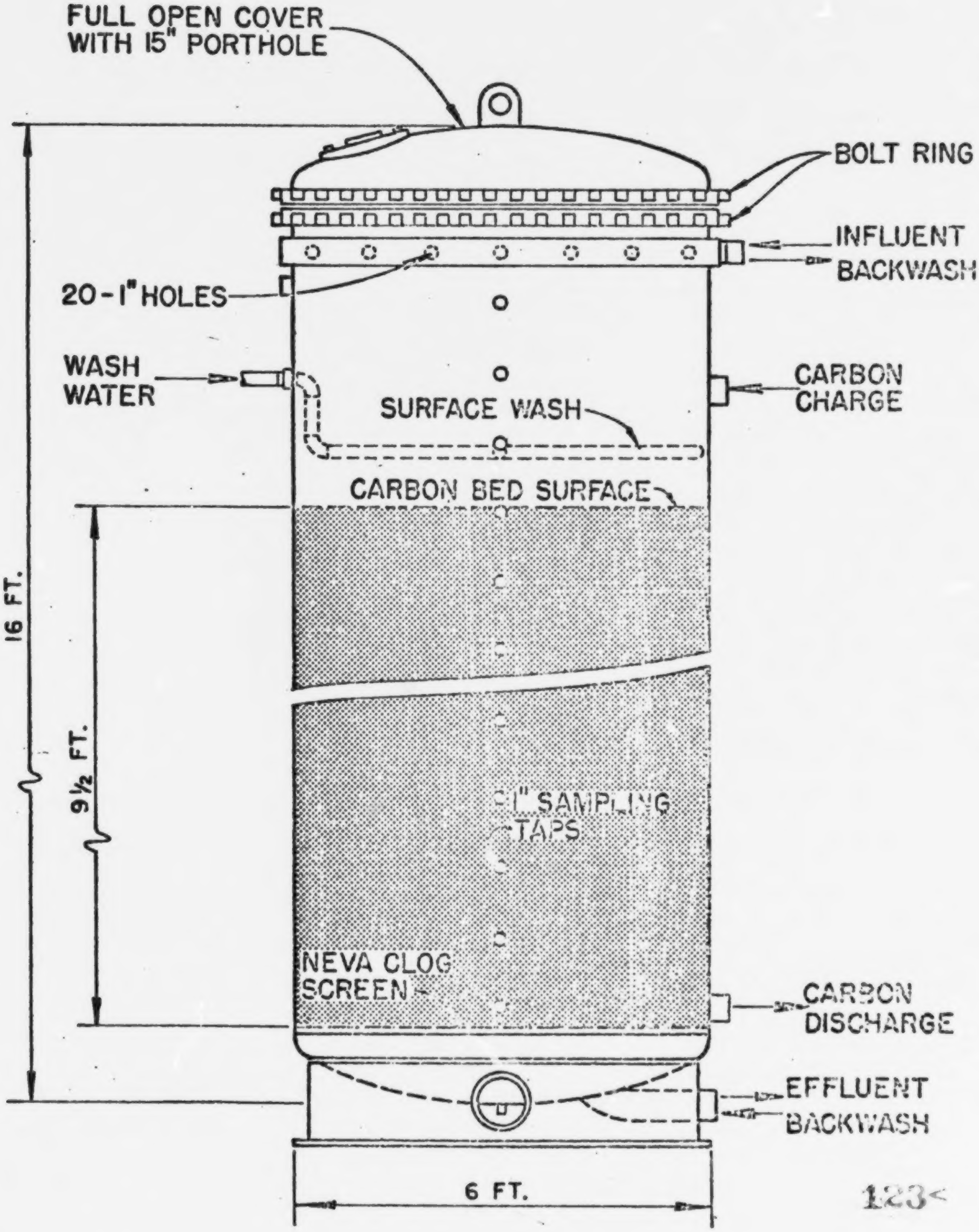
MASS ACCOUNTING OF PHOSPHORUS


TOTAL INPUT OF PHOSPHORUS
SUPERNATANT
WASTE SLUDGE
RAW WASTE H_2O
% NET INPUT OF PHOSPHORUS
100
80
60
40
20
0
PRIMARY EFFLUENT
HIGH RATE EFFLUENT
NITRIFIED EFFLUENT
FINAL EFFLUENT
REMOVE FROM SYSTEM
RECYCLE TO PRIMARY
RECYCLE TO PRIMARY
PRIMARY SLUDGE
A
WASTE SLUDGE
B
WASTE SLUDGE
C
D
A+B+C+D=
TOTAL INPUT
LEGEND
PHOSPHORUS PATHWAYS THROUGH PLANT
1. — - — - — LIQUID REGIME
2. - - - - - - - SLUDGES

MODIFICATIONS OF THE DENITRIFICATION PROCESS


I. OPEN TANK DENITRIFICATION
(ACTIVATED SLUDGE TYPE CULTURE)
HIGH-RATE
ORGANIC SYNTHESIS
NITRIFICATION
II. COLUMN
DENITRIFICATION
(FINE MEDIA)
SAND FILTER
OPTIONAL
III. COLUMN DENITRIFICATION
(COARSE MEDIA)

TYPICAL CONTACTOR


FULL OPEN COVER
WITH 15" PORTHOLE
BOLT RING
INFLUENT
BACKWASH
20-1" HOLES
WASH
WATER
CARBON
CHARGE
SURFACE WASH
CARBON BED SURFACE
16 FT.
9½ FT.
1" SAMPLING
TAPS
NEVA CLOG
SCREEN
CARBON
DISCHARGE
EFFLUENT
BACKWASH
6 FT.

PHYSICAL-CHEMICAL METHODS FOR NITROGEN REMOVAL

Joseph B. Farrell

I. INTRODUCTION

Nitrogen enters wastewater chiefly in the form of organic molecules of various degrees of complexity. Urea, the predominant form, is rapidly converted to the ammonium ion by enzymatic action. Conventional biological treatment may convert part of the ammonium ion to nitrate ion. The major proportion of nitrogen is present in the form of ammonium and nitrate ion, although smaller amounts of nitrite ion and nitrogen-containing organic molecules are found.

The physical and chemical methods used to remove ammonium and nitrate ions from wastewater are:

a. ammonia stripping

b. ion exchange

c. chemical destruction

The total nitrogen content of municipal wastewater averages about 20 mg/l (as N).

II. AMMONIA STRIPPING

In most activated sludge treatment plants, the nitrogen remaining in the final effluent is chiefly in the form of the ammonium ion. As such, it cannot be stripped from water by contact with air. When the pH is raised to approximately 11.0, the excess of hydroxyl ions converts the ammonium ion to ammonium hydroxide:

$$NH_4^+ + OH^- \rightleftharpoons NH_4OH \rightleftharpoons NH_3 + H_2O \qquad (1)$$

Bubbling air through the ammonium hydroxide solution will now remove ammonia.

A drawback of this process is the high solubility of ammonia in water. For example, it is over one thousand times more soluble in water than is carbon dioxide. In countercurrent contact at 20° C, the minimum air requirement to remove 90% of the ammonia from wastewater is about 220 cubic feet per gallon of water.

This high air-to-water ratio requires the use of stripping towers with very low pressure drops--essentially water-cooling towers. Another difficulty brought about by the high air requirement is poor cold weather performance. The wastewater is cooled by contact with air, increasing further the solubility of ammonia.

III. ION EXCHANGE

A. Ammonium Ion Removal

The ammonium ion can be removed by contact with a cation exchange resin. An example is shown in Figure 1. The reaction reaches an equilibrium when only part of the cations originally on the resin have been replaced. With the cation-exchange resins ordinarily available, selectivity for NH_4^+ over, for example, Na^+, is poor.

Certain zeolites show unusual selectivity for ammonium ion. Figure 2 shows a comparison of the selectivity of one of these zeolites for NH_4^+ compared to Ca^{++}. The fractional concentration of ammonium ion on the zeolite is compared with its fractional concentration in solution. At a given fraction of NH_4^+ in solution, the fraction of NH_4^+ on the ion-exchange material is much higher for the Hector clinoptilolite than for the conventional ion-exchange resin, IR 120. The Hector clinoptilolite shows a similar high selectivity for Mg and Na, but not for K.

B. Nitrate Ion Removal

The nitrate ion can be removed by contact with an anion exchange resin. See Figure 1 for an example. Anion exchange materials selective for nitrates have not as yet become available.

IV. CHEMICAL DESTRUCTION

A. Chlorination

The reactions showing nitrogen removal by chlorination are as follows:

$$3Cl_2 + 2NH_3 \longrightarrow N_2 + 6HCl \qquad (2)$$

$$NH_3 \xrightarrow{Cl_2} NH_2Cl \xrightarrow{Cl_2} NHCl_2 \xrightarrow{Cl_2} NCl_3 \qquad (3)$$

Chlorine requirements are high. Up to 10 mg chlorine are required per 1.0 mg ammonia nitrogen.

B. Ozonation

$$NH_3 + 4O_3 + OH^- \longrightarrow NO_3^- + 2H_2O + 4O_2 \qquad (4)$$

This reaction is not efficient at low concentrations. Also, it merely changes the form of nitrogen. However, for some purposes, nitrate ion is less objectionable than ammonium ion.

C. Reduction of Nitrate

Nitrate can be reduced by Fe^{++} by the following two paths:

$$2NO_3^- + 15FeSO_4 + 34H_2O \xrightarrow{Cu^{++}} 5Fe^{++}Fe_2^{+++}(OH^-)_8\downarrow + N_2\uparrow + 14H_2SO_4 + SO_4^{=} \qquad (5)$$

$$2NO_3^- + 24FeSO_4 + 58H_2O \xrightarrow{Cu^{++}} 8Fe^{++}Fe_2^{+++}(OH^-)_8\downarrow + 2NH_4^+ + 2SO_4^{=} + 22H_2SO_4 \qquad (6)$$

Reactions 5 and 6 go in about equal proportions.

Obviously, a cheap source of ferrous sulfate is required, and there must be a convenient means for disposing of the sludge. Possible area of use is for toxic chemical wastes and for low-temperature waters.

V. COSTS

A. Removal as NH_4^+ or NH_3

1. Stripping -- Approximately 2.3¢/1000 gal. If cost of lime is included, 5.0¢/1000 gal. Cost is not sensitive to total NH_3 content.
2. Chlorination -- Approximately 5.3¢/1000 gal. Cost is directly proportional to total NH_3 content.
3. Ion Exchange -- Approximately 8.0¢/1000 gal. with non-specific resin on carbon-treated water. Costs have not been estimated for selective zeolite. Cost is dependent on total NH_4^+ content.

B. Removal as Nitrate Ion

Additional aeration is usually needed to obtain nitrification. No cost has been assigned for this additional processing.

1. Ion Exchange -- About 18¢/1000 gal. on a secondary effluent (Eliassen). Cost is dependent on total NO_3 content.
2. Chemical Reduction -- No estimate available for ferrous sulfate process.
3. Biological Reduction -- About 3¢/1000 gal. (Barth).

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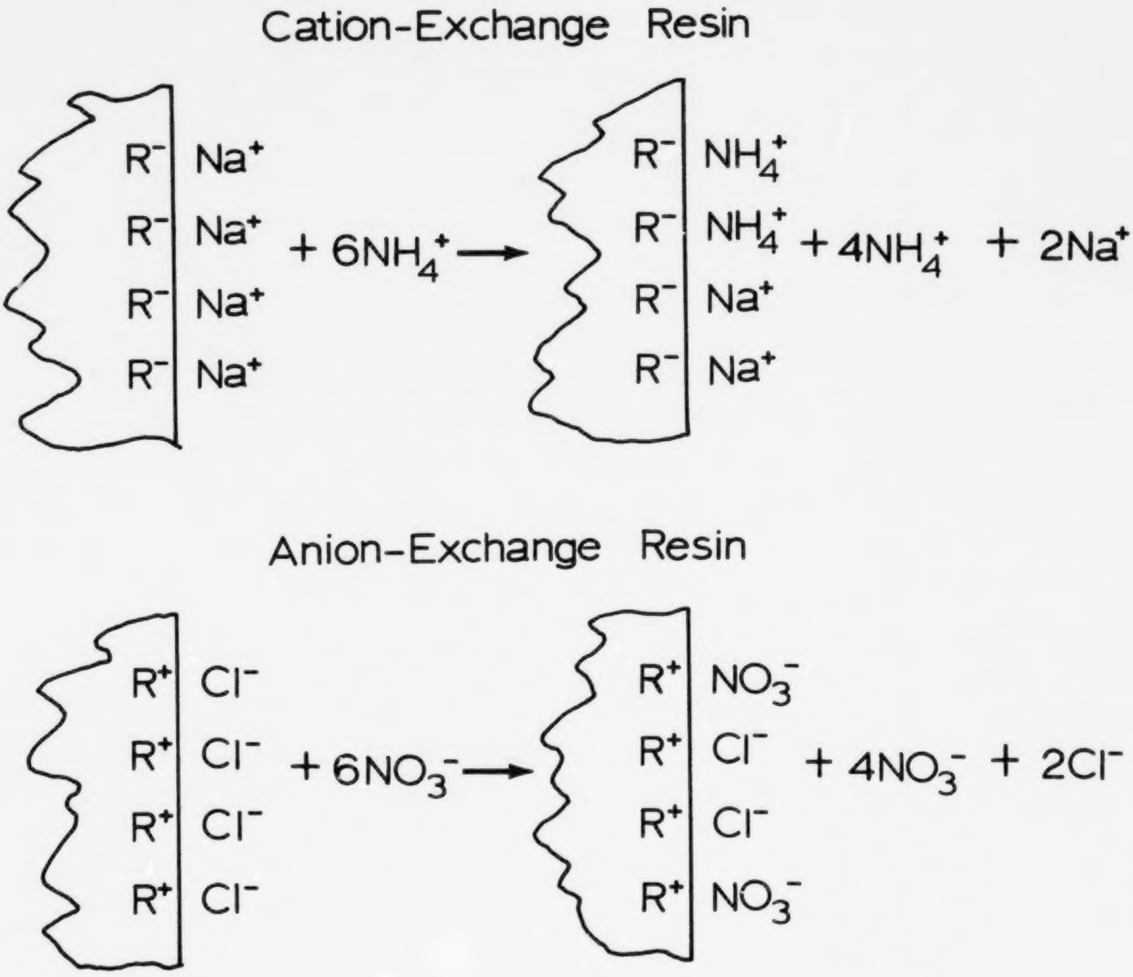
Cation-Exchange Resin
R⁻ Na⁺
R⁻ Na⁺
R⁻ Na⁺
R⁻ Na⁺
+ 6NH₄⁺ →
R⁻ NH₄⁺
R⁻ NH₄⁺
R⁻ Na⁺
R⁻ Na⁺
+ 4NH₄⁺ + 2Na⁺
Anion-Exchange Resin
R⁺ Cl⁻
R⁺ Cl⁻
R⁺ Cl⁻
R⁺ Cl⁻
+ 6NO₃⁻ →
R⁺ NO₃⁻
R⁺ Cl⁻
R⁺ Cl⁻
R⁺ NO₃⁻
+ 4NO₃⁻ + 2Cl⁻

FIGURE 1

REMOVAL OF IONS FROM AQUEOUS SOLUTION

BY MEANS OF ION-EXCHANGE RESINS

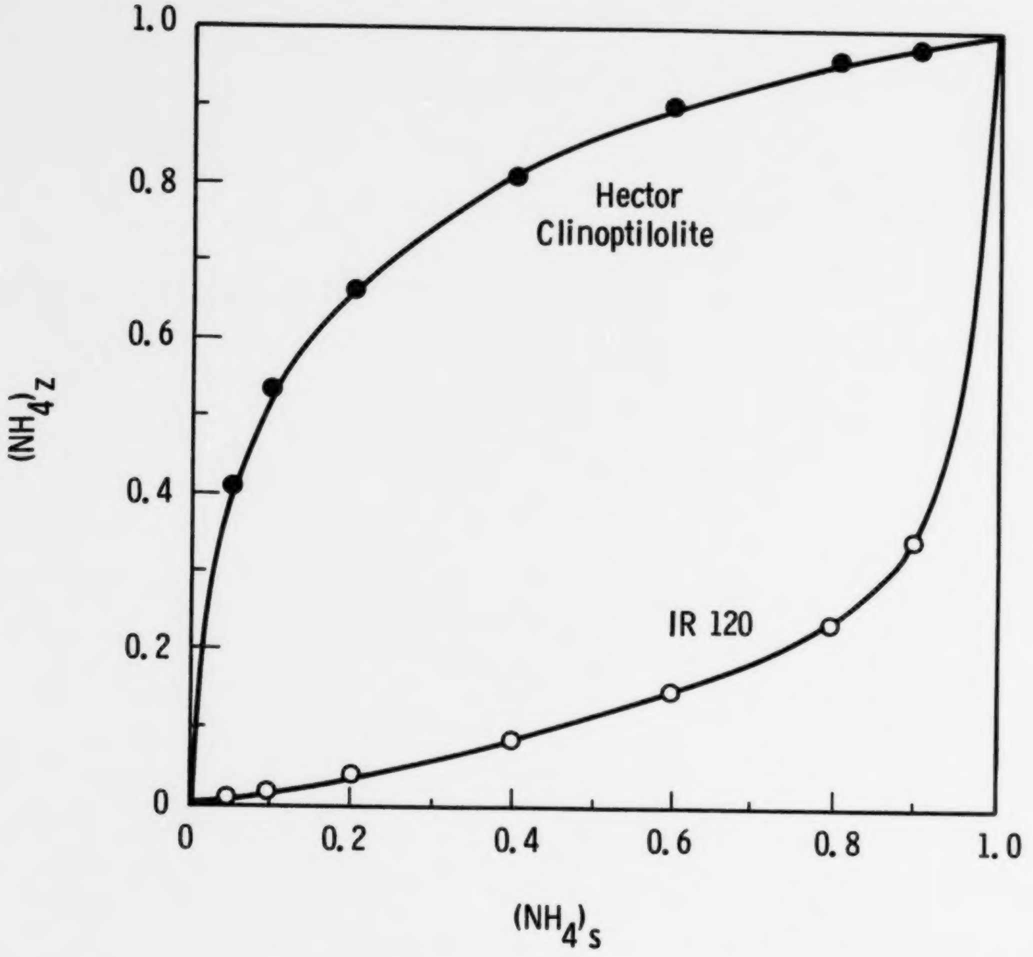

FIGURE 2

COMPARISON OF SELECTIVITY OF ION-EXCHANGE MATERIALS

23° C isotherms for the reaction, $(Ca)_{zeol.} + 2(NH_4)_{soln.} = 2(NH_4)_{zeol.} + (Ca)_{soln.}$ with Hector clinoptilolite and IR 120. Total equilibrium solution normality was constant at 0.1. The fractional concentration of NH_4^+ in the aqueous solution is plotted against its concentration on the zeolite.

THIRD TECHNICAL SESSION

Edgar N. Henry, Moderator

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METHODS FOR ACHIEVING HIGH BOD AND SOLIDS REMOVAL IN CONVENTIONAL PLANTS

Robert L. Bunch

I. INTRODUCTION

A properly designed and well-operated secondary biological treatment process needs no new technology to achieve suspended solids, BOD, and coliform removals in the range of 90-95%; what is needed is awareness of the fundamentals involved and a willingness to pay for and apply all we know.

Many secondary treatment plants are now operating near or over the design capacity both hydraulically and organically. Construction of all new plants cannot be undertaken immediately. In the meantime, what can be done to upgrade the existing plants? When plans are made for new treatment plants, what considerations should be made for future treatment processes? Some treatment plants will be able to achieve higher standards with only minor modifications, while with others, extensive changes will be necessary. The object of this talk is not to solve specific individual problems, but to discuss general suggestions you can carry back with you to be applied wherever applicable.

II. PROVIDING PROPER PLANT OPERATION

There are two main reasons why there are so many poorly-operated treatment plants:

A. The first reason is that the average city fails to realize the necessity of providing a competent and industrious plant operator to perform certain fundamental duties at the right time and in the right way. The difference between a poor operator and a certified, competent one can mean a tremendous difference in the overall effectiveness of a plant. Our Federal, State, and local governments have a clear responsibility to train and attract, and hold, good technicians and operators.

B. The second reason why there are so many poorly-operated treatment plants is that many city councils fail to provide yearly a sufficient repair and replacement fund. The municipal treatment plants of today are highly mechanized and represent a heavy investment of public funds. This investment should be protected by adequate budgets for continuing operation.

III. AIDING HYDRAULICALLY OVERLOADED PLANTS

A. Equalization Tank

The rate of flow of wastewater from any district varies with the season, the day, and the hour. These fluctuations of flow affect the operation of the treatment plant. If a plant is hydraulically overloaded, an equalizing or surge tank will smooth out the high peak flows. This tank should be aerated and not be considered as a settling basin.

B. Consider using large interceptors as holding tanks.

C. Find and reduce needless sources of wastewater.

D. Enlarge plant.

E. Numerous means are available to reduce discharged solids from overloaded plants both in process or by subsequent operations:

1. Chemical flocculation or precipitation.
2. Increased sedimentation capacity or improved inlet and/or overflow design.
3. Microscreening.
4. Sand filtration.
5. Flotation.

IV. AIDING ORGANICALLY OVERLOADED PLANTS

1. Equalization tank.
2. Chemical precipitation or flocculation of raw sewage.
3. Industry may program the load for slow or controlled release.
4. Industry may treat at the source by roughing filter, or by appropriate means to relieve part of the load.
5. Increased MLSS and air supply may be used during overload.

6. Treat digester supernatant return by alternate methods or program return load.

7. Baffle aeration tank to stop short-circuiting.

8. AWT treat part of final effluent and blend.

V. FUTURE DESIGN CONSIDERATIONS

A. Laboratory Control Space

It is unfortunate that in the past, designing engineers neglected to provide space for routine tests. Today, it is well known that the lack of proper laboratory controls will adversely affect the performance of any treatment plant, large or small.

B. Emergency Power Facilities

A standby power source should be provided so that raw sewage is not discharged or let backup in sewers until they overflow.

C. Automatic Control Equipment

The trend of sewage treatment processes is toward mechanization and automatic controls. These developments are becoming increasingly necessary, not only as a means of increasing the ease and efficiency of treatment, but also because the increasing difficulties experienced in obtaining labor for the more unpleasant and laborious duties in waste treatment.

D. Chemical Storage

Consideration should be given to providing a space for a future building to house chemicals. AWT treatment considered today, requires storage and handling of truckloads of precipitating agents, coagulants, and activated carbon.

E. Chemical Feeding

Improve degree of treatment required in the future will undoubtedly make use of chemical methods. Provision should be made in the plant layout so that much expense is saved in future extension.

F. Factor of Treatability

In the early days of waste treatment, plants were designed to deal primarily with domestic sewage. Experience with domestic sewage has dictated the design criteria in the past, but many industrial organic wastes do not have the same degree of amenability. For unknown wastes, the degree of amenability must be established before adequate design can be developed. Properly designed processes can make some undesirable wastes more amenable to biological treatment. Some wastes will cost less to treat if done separately at their origin while they are in a concentrated form.

CASE HISTORIES OF PLANT IMPROVEMENT BY OPERATIONS CONTROL

Alfred W. West

I. INTRODUCTION

A. Pollution can be greatly reduced, almost overnight, by maximum use of existing secondary treatment processes.

B. Activated sludge plants can produce final effluents containing considerably less than 10 mg/l suspended solids and 5-day BOD. Overall reductions of 95 to 99 percent are possible.

To obtain such results; the plants must be properly designed with adequate built-in capacity and flexibility; plant characteristics must be appropriate to the incoming load; and the process must be skillfully controlled by conscientious qualified operators.

II. SIOUX FALLS, SOUTH DAKOTA

A. Plant Description

Treats 3.5 mgd strong meat-packing waste and 6.0 mgd domestic sewage. High rate trickling filters pretreat packing plant wastes; activated sludge treats domestic sewage and polishes industrial wastes.

B. Feature Story - 99% Reductions

Has demonstrated ability to provide 99% reductions during summertime (August) when plant was operating within design loading (Figures 1 and 2). BOD reduced from 900 to 9; TSS from 650 to 5 (Figures 3 and 4).

C. Improved Operational Control

Wintertime pollutional load to river cut in half by improved operational control alone.

1. Control tests

Started using:

Settlometers for sludge density

Centrifuge for sludge density

Blanket finder for clarifier sludge blanket

Turbidimeter for current effluent quality

2. Interpretation

   Sludge condition, system equilibrium, and process demands are the key items for system control.

3. Control adjustments

   a. Increased return sludge percentage from 30% to more than 100%.

   b. "Tight-rope" sludge wasting control to increase sludge concentration and activity without upsetting aerators and clarifiers.

4. Improved effluent quality

   Former 30 mg/l BOD reduced to 20 mg/l

   Former 35 mg/l TSS reduced to 13 mg/l

D. Significant Loading Characteristics

See Table No. 1.

E. Favorable Features at the Existing Plant:

1. Dedicated supervision and operation
2. Efficient aerators (Not spiral flow)
3. Effective suction type final clarifier sludge removal mechanism
4. Complete mixed aerator flow pattern
5. Adequate return sludge pumping capacity

F. Plant Deficiencies

1. Activated sludge plant overloaded
2. Trickling filters freeze up in winter
3. Disproportionately small aerator/clarifier volume
4. Not enough air

TABLE NO. 1

SIGNIFICANT LOADING CHARACTERISTICS
(Sioux Falls, South Dakota - Activated Sludge Plant)

	SUMMER	WINTER
BOD Load to Aerators		
Pounds per day	18,000	37,400
Pounds per 1,000 cu.ft. Aerator	103	160
Pounds per pound mixed liquor solids	1.3	1.2
Clarifier Surface Loading Rate		
Gals./sq.ft./day	720	640
BOD Reductions		
Total - Trickling filter & activated sludge	99	97
Activated sludge alone	95	90
TSS Reductions		
Total - Trickling filter & activated sludge	99	96
Activated sludge alone	96	83

Air(Approximate Range)

12 to 36 million cu.ft./day
0.5 to 3.0 cu.ft./gal.
300-1,000 cu.ft./lb.BOD

Return Sludge - 30% to 200%

Aeration Detention Time - 1.5 to 3.0 hr.

5. No scum removers on final clarifiers

6. Impossible to make precise control adjustments. (Not enough meters, no remotely controlled mechanical valve actuaters, and no automatic sensor-controllers.)

III. METROPOLITAN ST. LOUIS SEWER DISTRICT - MSD

Coldwater Creek Wastewater Treatment Plant(Activated Sludge)

A. Basically, this is a conventional 21 mgd standard rate activated sludge plant.

There are 6 aerators with spiral flow pattern diffusers and 4 final clarifiers with plow-type sludge scrapers.

B. Feature Story - Pollution reduced to 1/4 its former strength by operation control alone.

1. Suspended Solids

		Before	After
Raw	(mg/l)	173	198
Primary Effluent	(mg/l)	155	142
Final Effluent	(mg/l)	92	16
Activated Sludge Reduction		40%	89%
Total Plant Reduction		46%	92%

2. 5-Day BOD

		Before	After
Raw	(mg/l)	150	162
Primary Effluent	(mg/l)	152	130
Final Effluent	(mg/l)	40	9
Activated Sludge Reduction		74%	93%
Total Plant Reduction		73%	94%

C. Improved Operational Control

1. Changed aerator/clarifier ratio: - by taking one of the 4 clarifiers out of service and placing an additional aerator in service. Theoretical full load characteristics as follows:

	Former	Changed To
Aerator/Clarifier Combination	3A/4C	4A/3C
Mixed Liquor(% by Centrifuge)	7.2	3.4
Return Sludge(% of Sewage Flow)	93	30
Flow Capacity (MGD)	13.2	14.5
Aerator Detention (HRS)	3.0	5.4
Clarifier Detention (HRS)	2.0	2.0

2. Control Tests & Interpretation

   Introduced use of settlometers, centrifuge, blanket finder and turbidimeter to detect process balance and demands.

3. Control Adjustments

   In this case: Reduced return sludge pumping. Increased air supply and excess sludge-wasting rates.

E. Favorable Features at the Existing Plant

   1. Dedicated supervision and operation
   2. Adequate plant capacity for present dry weather flow
   3. Multiple unit aerator and clarifier groups

F. Plant Deficiencies

   1. Plow-type sludge scrapers in final clarifiers
   2. Spiral flow diffuser placement in aerators
   3. Hydraulic short circuiting plus strong velocity currents in final clarifiers
   4. No scum removal for final clarifiers
   5. Inadequate return sludge capacity
   6. Meter problems, and lack of remotely controlled mechanical valve actuators or automatic sensor-controllers limit process controlability.

G. Present Status

   1. Presently obtaining 90% reductions
   2. Could cut pollutional load in half again if obvious plant deficiencies were corrected.

IV. CONCLUSIONS

A. The activated sludge process can produce sparkling clear final effluents.

Plants can and should be properly designed (or modified) and operated to obtain their maximum inherent purification efficiencies needed to abate pollution of our national water resources. These include:

B. Design

1. Provide adequate capacity for growth and equipment outages.

2. Flexibility - (Give the operators a chance.)

   Provide ability to increase or decrease number of aerators or clarifiers, convert to a complete mixed system or to step aeration as required.

3. Avoid "spiral flow" aeration.

4. Use suction devices in final clarifiers for rapid removal of fresh sludge. Also provide surface scum removers.

5. Make air supply, sludge return and sludge wasting equipment truly variable and conveniently controllable.

6. Provide essential meters and sensors, remote valve actuators and automatic ratio controllers where required.

C. Operation

1. Recruit and retain conscientious, intelligent, trained, and certified plant operators.

2. Provide practical "on-the-job" work experience type training.

3. Provide 24-hour around-the-clock operation. Test, evaluate and adjust process at least once per 8-hour shift.

4. Make the best use of existing facilities, guide counsel, and consulting engineers in designing needed improvements and additions.

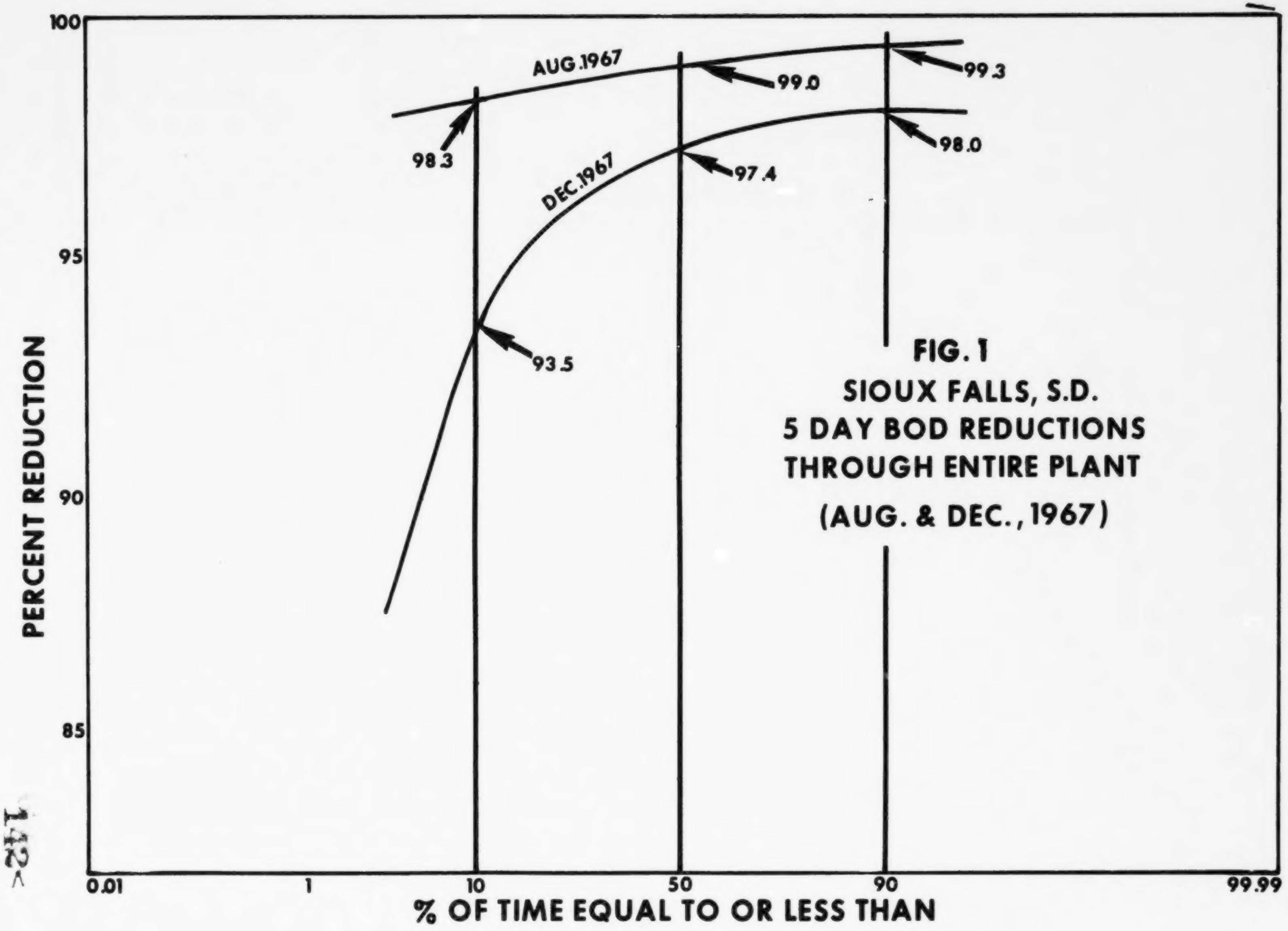

FIG. 1
SIOUX FALLS, S.D.
5 DAY BOD REDUCTIONS
THROUGH ENTIRE PLANT
(AUG. & DEC., 1967)

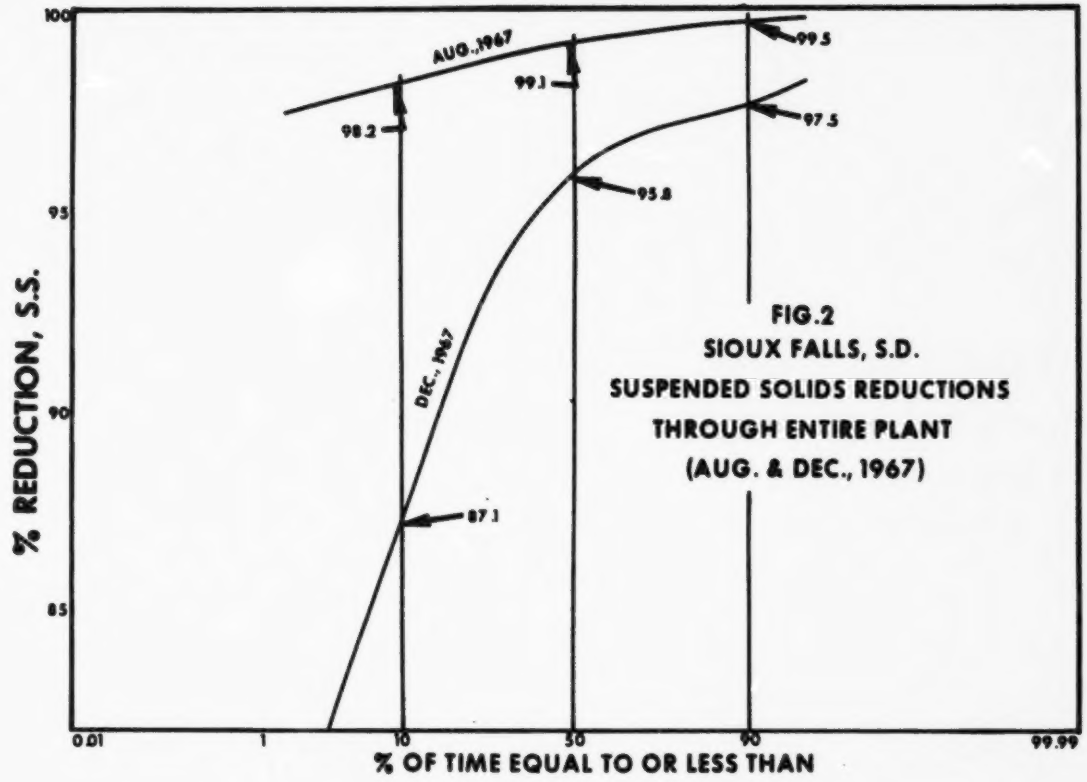

FIG.2
SIOUX FALLS, S.D.
SUSPENDED SOLIDS REDUCTIONS
THROUGH ENTIRE PLANT
(AUG. & DEC., 1967)

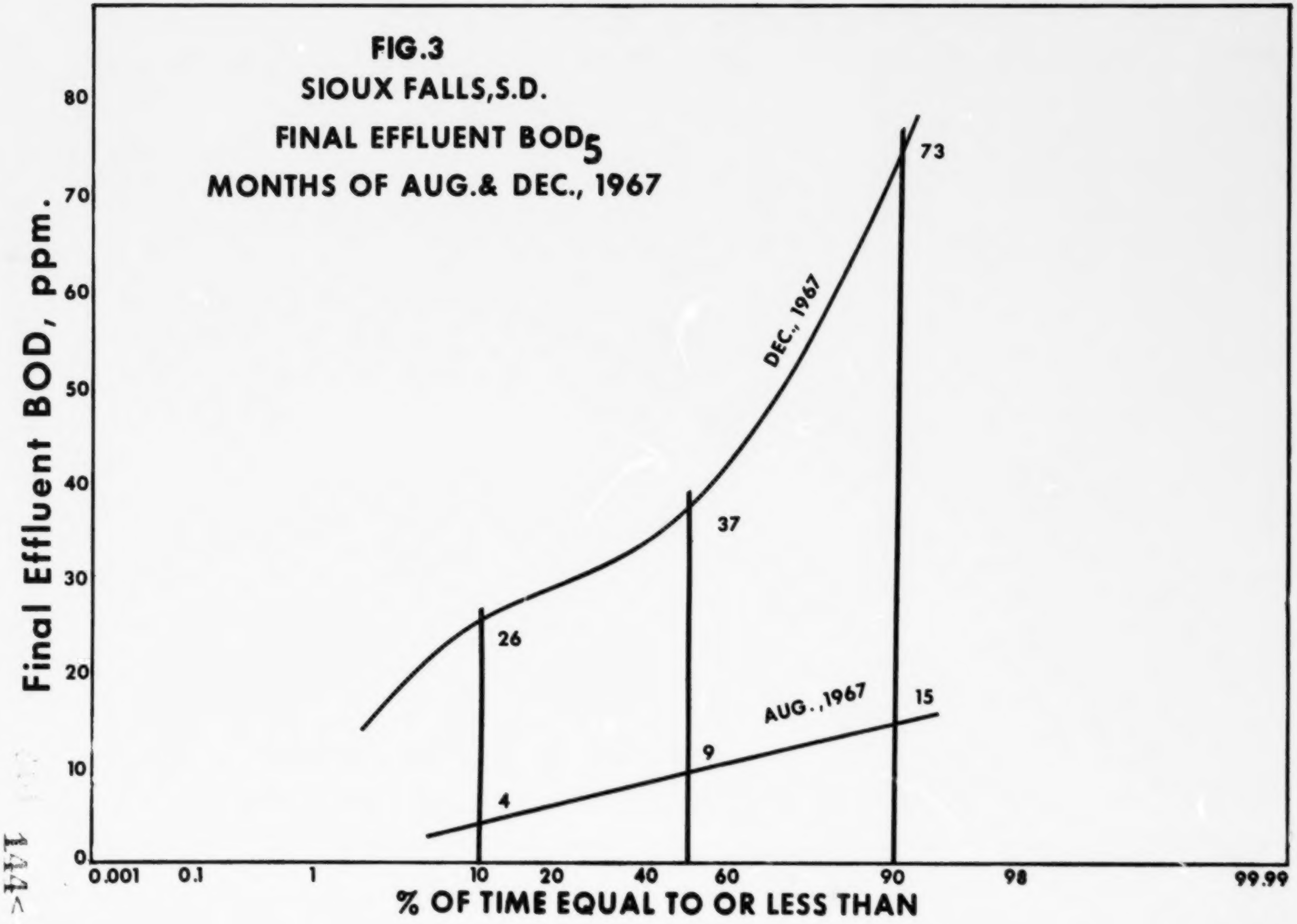

FIG.3

SIOUX FALLS,S.D.

FINAL EFFLUENT BOD_5

MONTHS OF AUG.& DEC., 1967

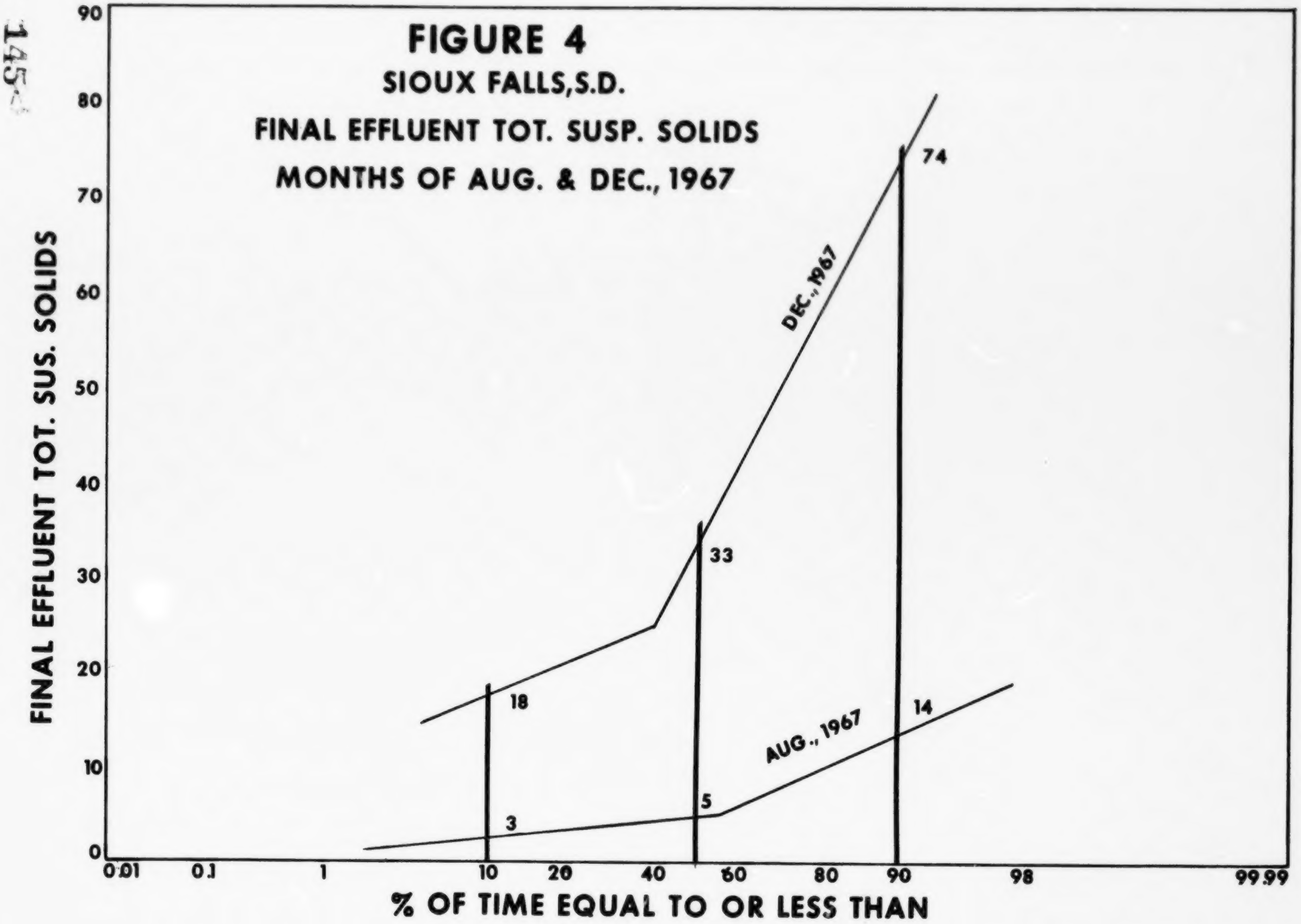

FIGURE 4

SIOUX FALLS,S.D.

FINAL EFFLUENT TOT. SUSP. SOLIDS

MONTHS OF AUG. & DEC., 1967

SOLIDS REMOVAL PROCESSES

John J. Convery

I. Screening Devices*

A. Functional Description

Microscreening is a form of simple filtration. These mechanical filters consist of a rotary drum which revolves on a horizontal axis. The peripheral surface of the drum is covered with a stainless steel filter fabric. The effectiveness of the woven mesh screen for retaining fine particles is dependent on the size of openings in the screen and on the pattern of the weave employed. Influent enters the open end of the drum and is filtered through the fabric with the intercepted solids being retained on the inside surface of the fabric. As the drum rotates, the solids are transported and continuously removed at the top of the drum by pumping strained effluent, under pressure, through a series of spray nozzles which extend the length of the drum. The solids and wash water are collected in a central trough within the drum and discharged through a hollow axle. Some mechanism such as intermittent chlorination (every 3 to 8 days), or continuous ultraviolet lighting must be employed to prevent the growth of biological slimes on the fabric.

B. Physical Description

A typical microstraining unit is shown in Figure 1.

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*Comments and operating experience refer to the patented Micro-Strainer, a product of Glenfield and Kennedy, Ltd., London, England. Mention of a proprietary name is not an endorsement by FWPCA.

1. Unit Sizes and Capacity[8]

Drum Sizes in Feet Diameter	 Width	Approx. Capacity mgd
5	1	0.05 - 0.5
5	3	0.3 - 1.5
7½	5	0.8 - 4
10	10	3 - 10

2. Fabric Details
See Table 1

C. Design Basis

The basic design criteria for the proper sizing of a microscreening unit is the filterability index, I. A device called the filtrameter[1] is available from Glenfield and Kennedy, Inc. for the field measurement of the filterability index I. This index is an expression of the volume of water obtained per unit headloss when passed at a standard rate through a unit area of standard filter fabric. The index is used to calculate the required area to treat a given flow of a specific wastewater according to the following expression:

$$H = \frac{mQC_f e^{nIQ/S}}{A}$$

where:

H = headloss, in.
Q = rate of flow, gpm
C_f = initial fabric resistance, sec.
A = effective submerged filter area, ft^2
I = filterability index, ft^{-1}
S = speed of rotation, area per unit time entering the water, ft^2/min.

The unit conversion factors m and n have values of 0.0267 and 0.1337, respectively. C_f is 1.8 sec. for the Mark O fabric and 1.0 sec. for the Mark I fabric.

TABLE 1

CHARACTERISTICS OF THREE FILTER FABRICS

	Mark O	Mark I	Mark II
Apertures:	1/1000 23 microns	1.5/1000 35 microns	2.5/1000 60 microns
No. per sq. in.:	160,000	80,000	60,000
No. per lineal in.:	400	280	240
Warp:	120 mesh 2 wires .0018	76 mesh 2 wires .0024	60 mesh 2 wires .0040
Weft:	600 mesh 1 wire .0016	500 mesh 1 wire .0022	420 mesh 1 wire .0028

D. Operating Parameters

1. Headloss

Microscreening devices should be installed at an elevation permitting gravity flow thereby eliminating the possible fractionation of flocculant particles. Experience has demonstrated that the removal efficiency of particulates is reduced when flocculant material is pumped.[2] The maximum operating headloss across the screen is normally limited to six (6) inches to prevent rupture of the delicate filter fabric.

2. Drum Speed

Some flexibility of operation can be achieved by varying the speed of rotation, S. Peripheral velocities normally range from 25 to 135 ft/min.

3. Wash Water Requirements

The function of backwashing is to thoroughly clean the filter fabric during each revolution with a minimum of wash water. Pressure appears to be more critical than the quantity of wash water to effect the cleaning. Wash water pressures range from 20 to 55 psi and water requirements are less than 5% of the throughput. The wash water is normally recirculated to the head end of the plant. The suspended solids concentration of the wash water approach 750 mg/l.

E. Performance in a Tertiary Treatment Application

1. Removal Efficiency and Flow Rate[8]

The effect of aperture size on removal efficiencies and flow rate are shown in the following table:

Fabric	Removal Solids	Efficiency BOD	Flow Gals./Hr/Ft^2
Mark O (23 microns)	70-80%	60-70%	400
Mark I (35 microns)	50-60%	40-50%	600

2. Operating Problems

The Federal Water Pollution Control Administration has conducted a study[3] of microscreening at Lebanon, Ohio. The secondary effluent from the municipal activated sludge treatment plant had an average suspended solids concentration of 17 mg/l while the Mark O fabric was tested and 27 mg/l during tests of the Mark I fabric. The filterability index, coincidentally, was 17.0 during both tests.

One of the major problems associated with operation of the microscreen was the unit's inability to handle wide fluctuations in solids loadings. On one occasion the solids in the feed increased 8 fold from 25 to 200 mg/l. Within minutes the throughput of the unit was reduced from 60 to 13 gpm (21.7% of rated capacity). Figure 2 shows a frequency distribution of suspended solids values in the Lebanon secondary effluent.

Suspended solids concentrations in excess of 50 mg/l occurred 10% of the time. If the microscreening unit can produce 25% of its rated capacity during periods of high solids loading, (> 50 mg/l) 75% of the design flow must come from storage 10% of the time. Therefore, the plant must have an excess design capacity of 8.33%. A recent design improvement has been the coordination of drum speed and wash water pressure with changes in headloss across the fabric.

3. Limitations

Fine fabric microscreening is not recommended for the treatment of waters with a chloride content greater than 500 mg/1 because of potential corrosion problems.

F. Capital and Operating Costs

The capital and operating costs associated with microstraining of secondary effluent have been prepared by Smith[10] and are shown in Figure 3.

II. Coarse Media Filtration: Upflow and Downflow Configurations Compared

A. Description

The upflow coarse media filter is somewhat similar in appearance to the conventional rapid sand filter except that the direction of flow is upward. Backwashing in an upward direction grades the filter media with the coarser media on the bottom and finer media on the top. During filtration the effluent contacts progressively finer media and the intercepted solids are distributed throughout the filter bed rather than being concentrated near the surface. This uniform distribution of headloss and successively finer filtration are the reasons for the longer filter runs and improved product quality normally associated with in-depth filtration.

Upflow coarse media filters consist of 5 feet of 1-2 mm sand supported on progressively coarser layers of gravel and a distribution system. Total height is approximately 12 feet. A metal grid, consisting of parallel bars spaced 4 in. apart placed 2 in. below the surface of the bed, is used to prevent expansion of the filter media at flow rates as high as 6.7 gpm/ft^2. The backwash rate of 11.7 gpm/ft^2 is sufficient to expand the bed to permit cleaning. A wash cycle of 15 minutes was found adequate to clean the filter.

B. Performance

1. Activated Sludge Secondary Effluent

The solids concentration of the activated sludge effluent varied from 10 to 34 mg/1. The effluent from the upflow coarse media filter contained from 3.2 to 10 mg/l of suspended solids. The coarse media filter removed on the average 60% of the suspended solids and 53% of the BOD. The removal efficiency of a filter is a function of the hydraulic loading as shown in the following table:

Filtration Rate gph/ft^2	Removal Efficiency, % Suspended Solids
175	77
250	58
350	38

The longest length of run was 19.2 hours at a filtration rate of 200 gph/ft^2. Wash water consumption ranged from 4.6 to 6.7 percent of the filter throughput. The authors did not mention what terminal headloss was used to initiate the automatic backwash mechanism but they do indicate it was set too low. Therefore, extended filter runs and lower wash water consumption may be obtainable.

A microstraining unit with a Mark 0 fabric was operated in parallel with the upflow filter during this study. Results indicated that the filter effluent was superior to the strainer effluent at a filtration rate of 200 gph/ft^2 or less. Performance was comparable at the intermediate filtration rates of 200 to 400 gpm/ft^2. The microstrainer was operated at 260 gpm/ft^2. Filter performance was inferior to strainer performance at a filtration rate of 400 gph/ft^2 or more.

2. Trickling Filter Secondary Effluent

Naylor, et al, evaluated upflow and downflow media filtration of settled trickling filter effluent. The upflow filter had 5 feet of 0.9 mm to 1.7 mm sand and was operated at flow rates of 100 to 350 gph/ft^2. The downflow filter had only three feet of similar media. The secondary effluent suspended solids concentration ranged from 19 to 25 mg/l. The solids concentration of the filtered effluents ranged from 3.0 to 6.5 mg/l. The solids removal efficiency of the upflow filter as a function of filtration rate is shown in Figure 3A. These results are representative of short-term testing with a clean filter. Longer term operating results indicated that these high removal efficiencies could not be maintained at the higher filtration rates because of sloughing of material that developed within the filter media. Operating results for the months of January through March for both the upflow and gravity filters operating in parallel are shonw in the following table:

Month	Filtration Rate gph/ft^2	Secondary Effluent		Filter Effluent			
				Upflow		Downflow	
		BOD	S.S.	BOD	S.S.	BOD	S.S.
January	240	5.3	12.8	2.6 (51)	5.7 (55.5)	3.1 (41.5)	7.5 (41.4)
February	170	10.4	28.5	2.6 (75)	5.3 (81.5)	4.2 (59.6)	9.5 (66.6)
March	170	9.8	34.8	2.5 (74)	5.0 (85.5)	3.1 (68.5)	8.5 (75.5)

( ) Denotes removal efficiency

These results, together with the data reported by Truesdale, et al[12] are shown in Figures 3B and 3C.

The upflow filter configuration produced a better effluent than the downflow filter. This can be attributed to both the increased filter depth and improved media gradation. Thorough backwashing of the filters was essential to good operation. Both filters were air scoured and backwashed for 5 minutes at 750 gph/ft^2 during the cleaning cycle. The upflow filter required 26 minutes to clean and the downflow filter required 40 minutes. A backwashing frequency of once a day was adequate at a filtration rate of 200 gph/ft^2.

One significant factor, repeatedly reported in the literature pertaining to effluent polishing by any of the means described is the effect of the secondary effluent BOD concentration. High effluent BOD concentrations increase the problem of slime growths which necessitates more frequent backwashing. Tertiary removal of solids and associated BOD is not a substitute for good secondary treatment.

One advantage of the coarse media filtration is the availability of some floc storage capacity within the interstices of the filter media to permit partial phosphorus removal by chemical pretreatment.

The practice of chemical addition to the microstrainer influent has not been successful. The fragile floc breaks up on the screen.

C. Costs

The capital and operating costs for filtration through sand or graded media at 4 gpm/ft^2 has been estimated by Smith[10] and are shown in Figure 4.

III. Moving Bed Filter Technique

A. Description

The Moving Bed Filter (MBF) is a new tertiary solids and phosphorus removal technique that is currently being developed by Johns-Manville Products Corporation.* Evaluation of a pilot unit is currently being supported under contract by the FWPCA. A schematic diagram of the Moving Bed Filter is shown in Figure 5.

This unit is basically a sand filter. Particulate matter in the water is removed as the water passes through the sand (.6 - .8 mm). As the filter surface becomes clogged, the filter media is moved forward by means of a mechanical diaphragm. The clogged filter surface is hydraulically removed thereby exposing a clean filter surface. The sand and accumulated sludge is washed and the sand is returned to the base of the filter. The unit is thus a form of countercurrent extraction device feeding sand countercurrent to the water being filtered. The Moving Bed Filter has a renewable filter surface analogous to the microstrainer and the advantage of depth filtration comparable to the coarse media filter. The unit does not have to be taken off stream for backwashing. In theory, 1% of the filter is being backwashed 100% of the time compared to the conventional practice of backwashing 100% of the filter 1% of the time. External and more thorough cleaning of the filter media may prove to be an important factor in minimizing problems associated with slime growths.

B. Performance

The pilot MBF unit has been installed at the Bernards Township Plant in New Jersey to treat settled and unsettled trickling filter effluent and primary effluent. The pilot plant evaluation has just been initiated. The system lends itself well to the use of chemical aids ahead of filtration because of designed flexibility to handle high solids loadings.

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*Mention of a proprietary device does not indicate endorsement by the FWPCA.

Some very preliminary operating results obtained during the equipment development stage while treating unsettled trickling filter effluent are as follows:

ALUM DOSE	COAG. AID	TURBIDITY JTU			BOD mg/1			COD mg/1			TOTAL PHOSPHATE mg/1		
mg/1	mg/1	Inf.	Eff.	% Red.	Inf.	Eff.	% Red.	Inf.	Eff.	% Red.	Inf.	Eff.	% Red.
200	0	41	10.0	76	40	8.8	78	120	40	66	36	1.5	96
200	0.5	40	6.3	85	49	9.7	80	143	39	73	36	2.5	93
200	1.0	22	9.2	57	46	10.0	79	111	42	62	40	1.8	96
100	0.5	28	8.4	64	64	9.7	79	172	43	65	30	1.7	94

Of particular interest is the excellent phosphate removal obtained with 100 mg/1 of alum. This represents an AL/P ratio of about 1. Chemical requirements to produce a filterable floc may be significantly less than those required to produce a settleable floc.

It is too premature to even suggest a treatment cost for the Moving Bed Filter. Design and performance information developed from the Johns-Manville-FWPCA contract will be analyzed to project capital and O&M costs for comparison with alternate treatment processes.

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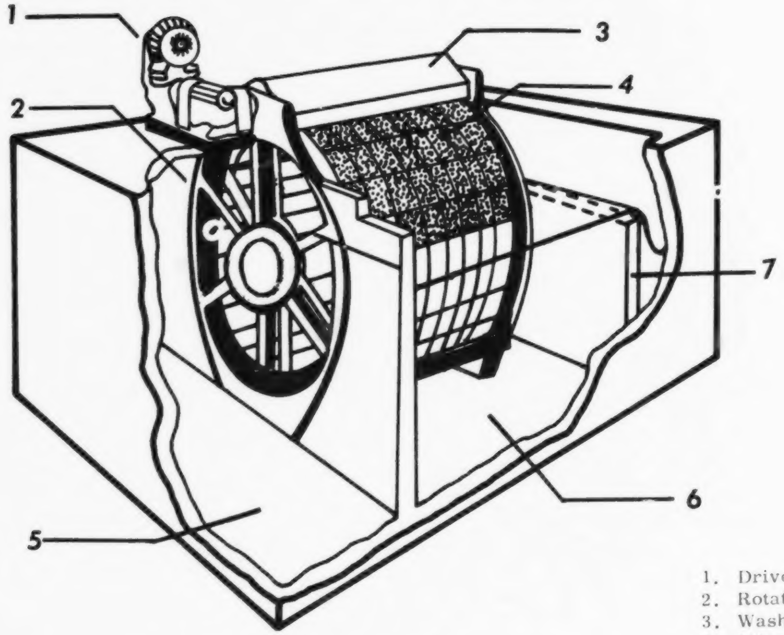


Fig. 1 Typical Microstrainer Unit

1. Drive Unit
2. Rotating Drum
3. Wash-water Jets
4. Micro-fabric
5. Influent Chamber
6. Effluent Chamber
7. Effluent Weir

Not Shown

Wastewater Hopper
Ultra-violet Lamp
Wash-water Pump

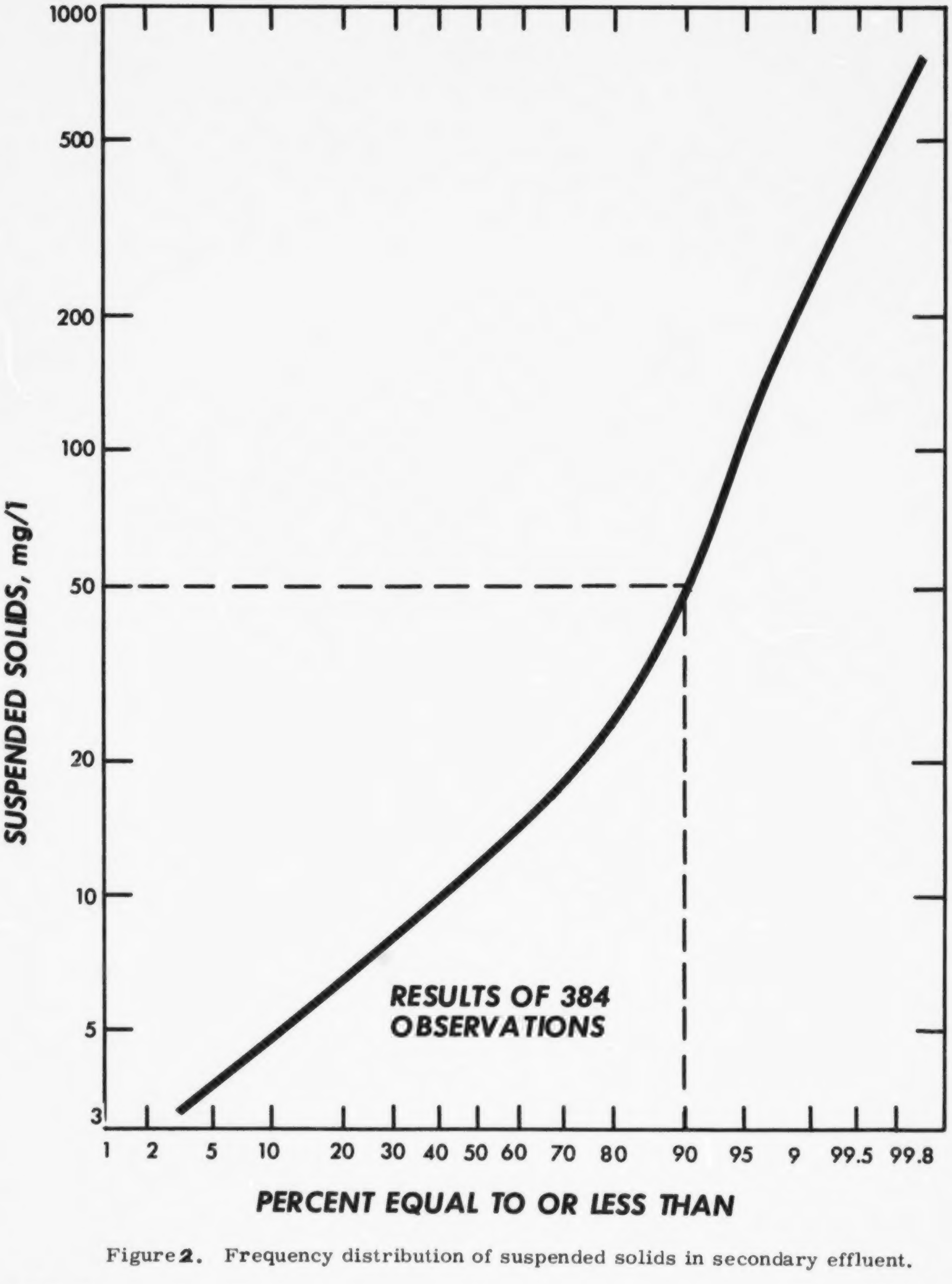
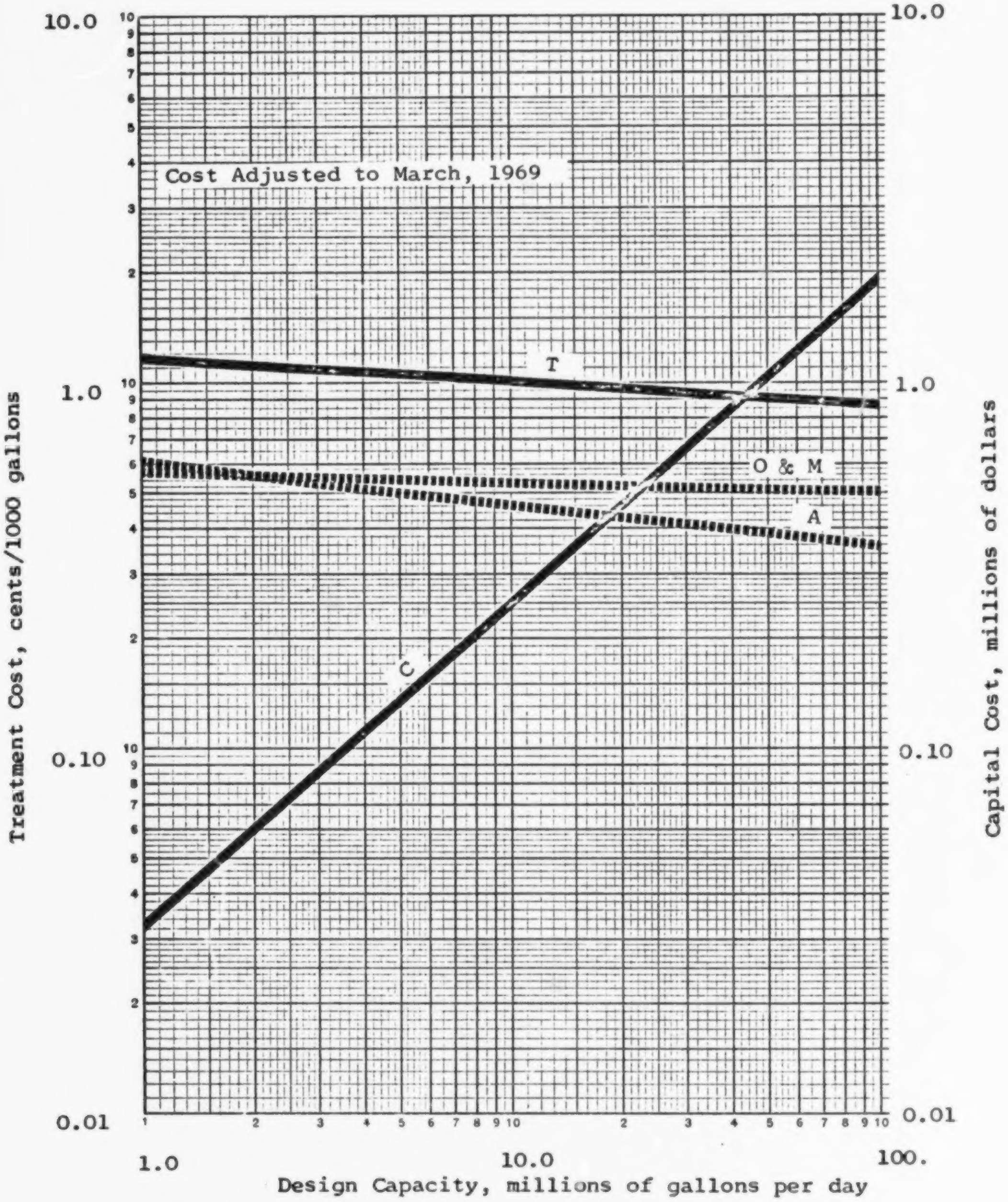


Figure **2**. Frequency distribution of suspended solids in secondary effluent.

MICROSCREENING OF SECONDARY EFFLUENT

Capital Cost, Operating & Maintenance Cost, Debt Service
vs.
Design Capacity



C = Capital Cost, millions of dollars
A = Debt Service, cents per 1000 gallons (4½% - 25 yr.)
O & M = Operating and Maintenance Cost, cents per 1000 gallons
T = Total Treatment Cost, cents per 1000 gallons

FIGURE 3

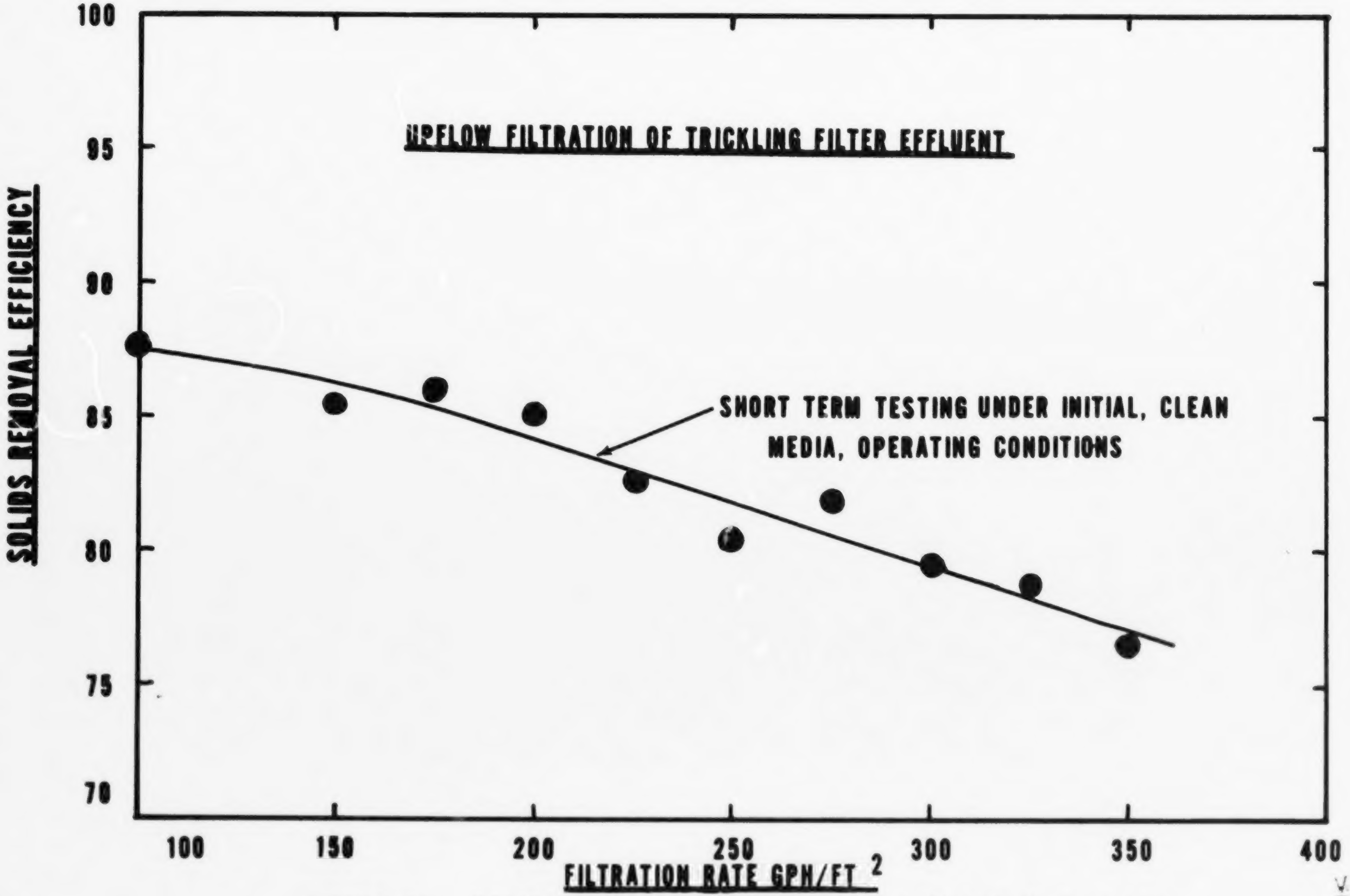


FIGURE 3A SOLIDS REMOVAL EFFICIENCY AS A FUNCTION OF RATE

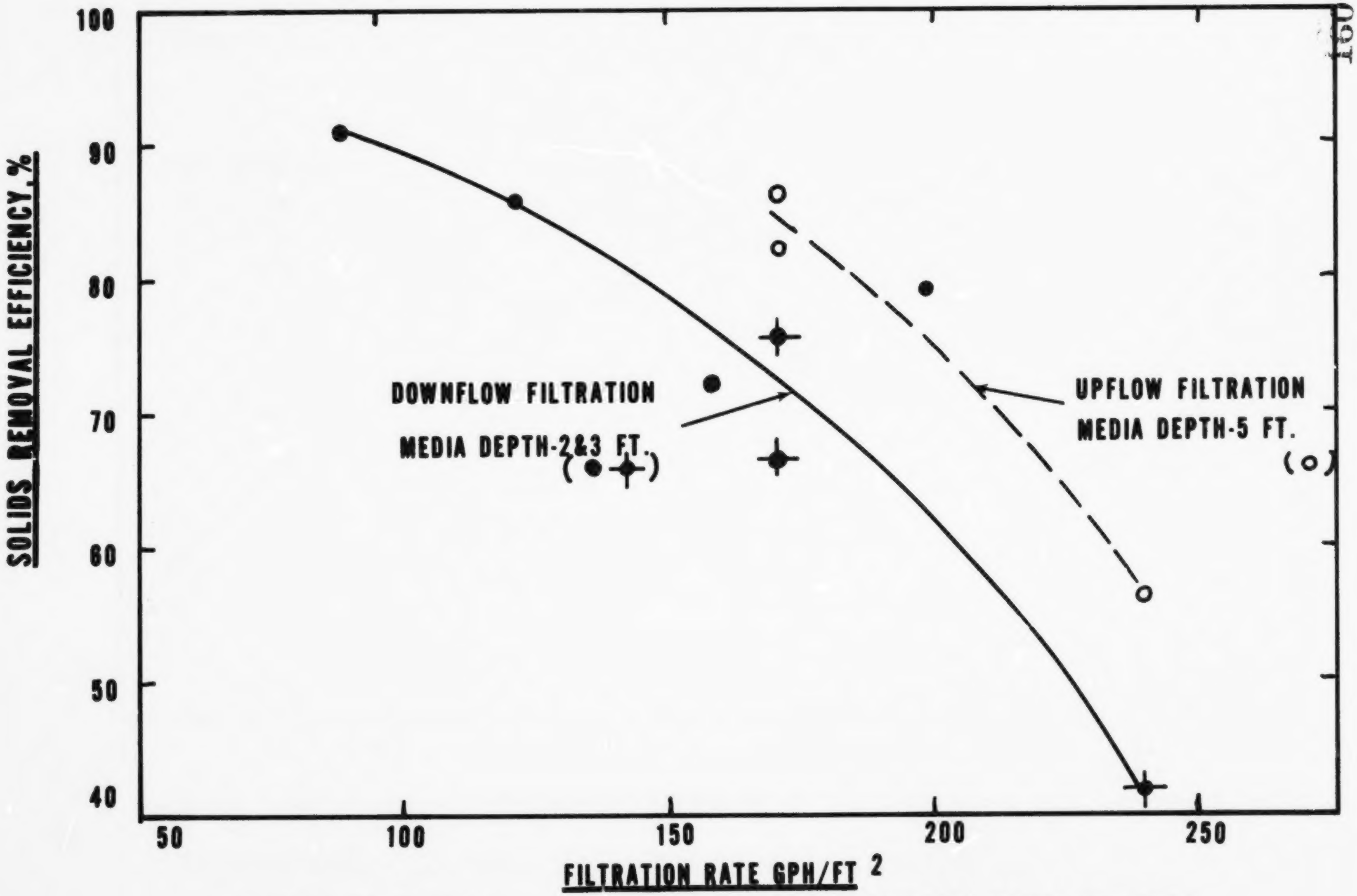


FIGURE 3B TERTIARY SOLIDS REMOVAL FROM TRICKLING FILTER EFFLUENT

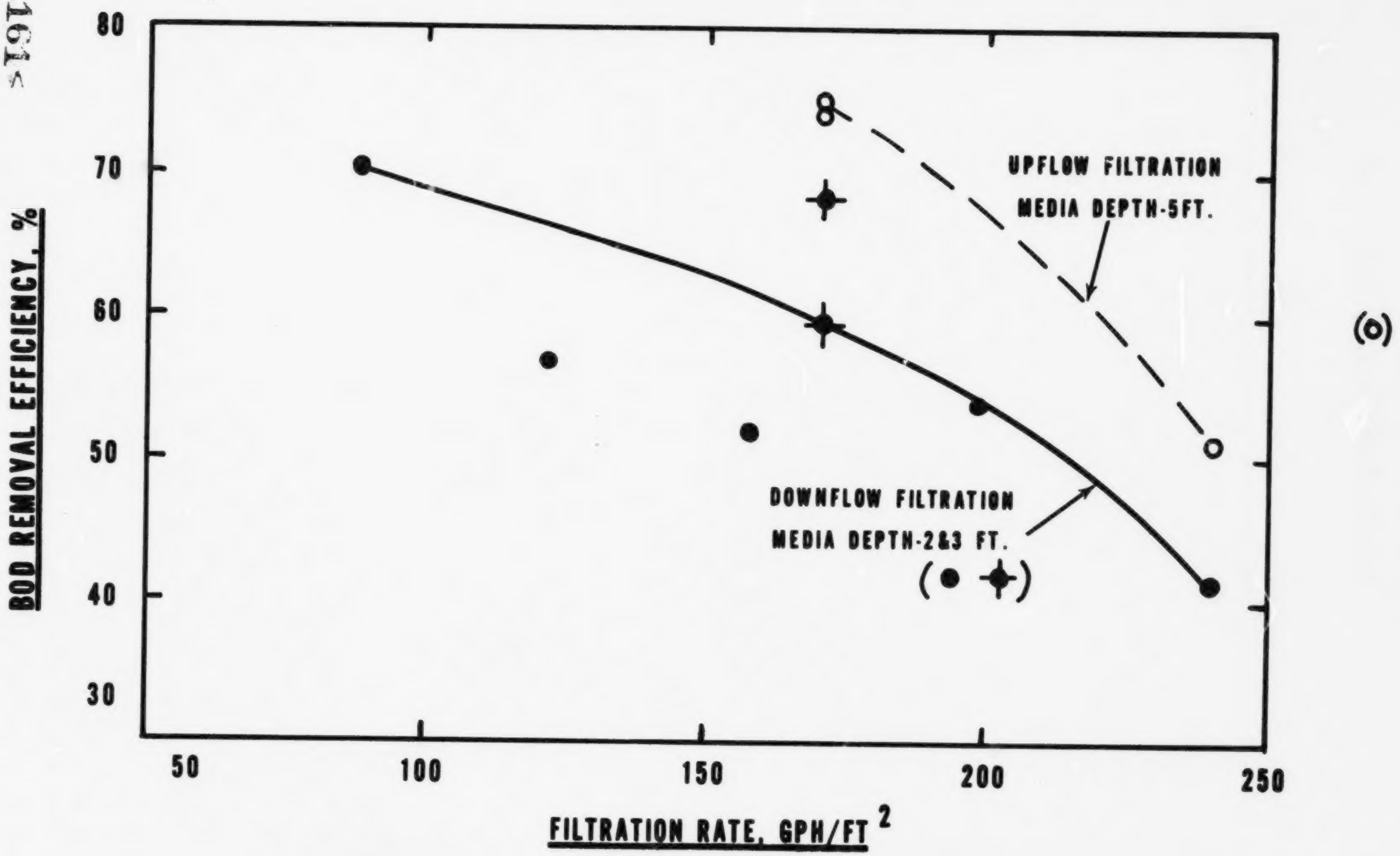


FIGURE 3C TERTIARY BOD REMOVAL FROM TRICKLING FILTER EFFLUENT

FILTRATION THROUGH SAND OR GRADED MEDIA - 4GPM/SQ FT

Capital Cost, Operating & Maintenance Cost, Debt Service
vs.
Design Capacity

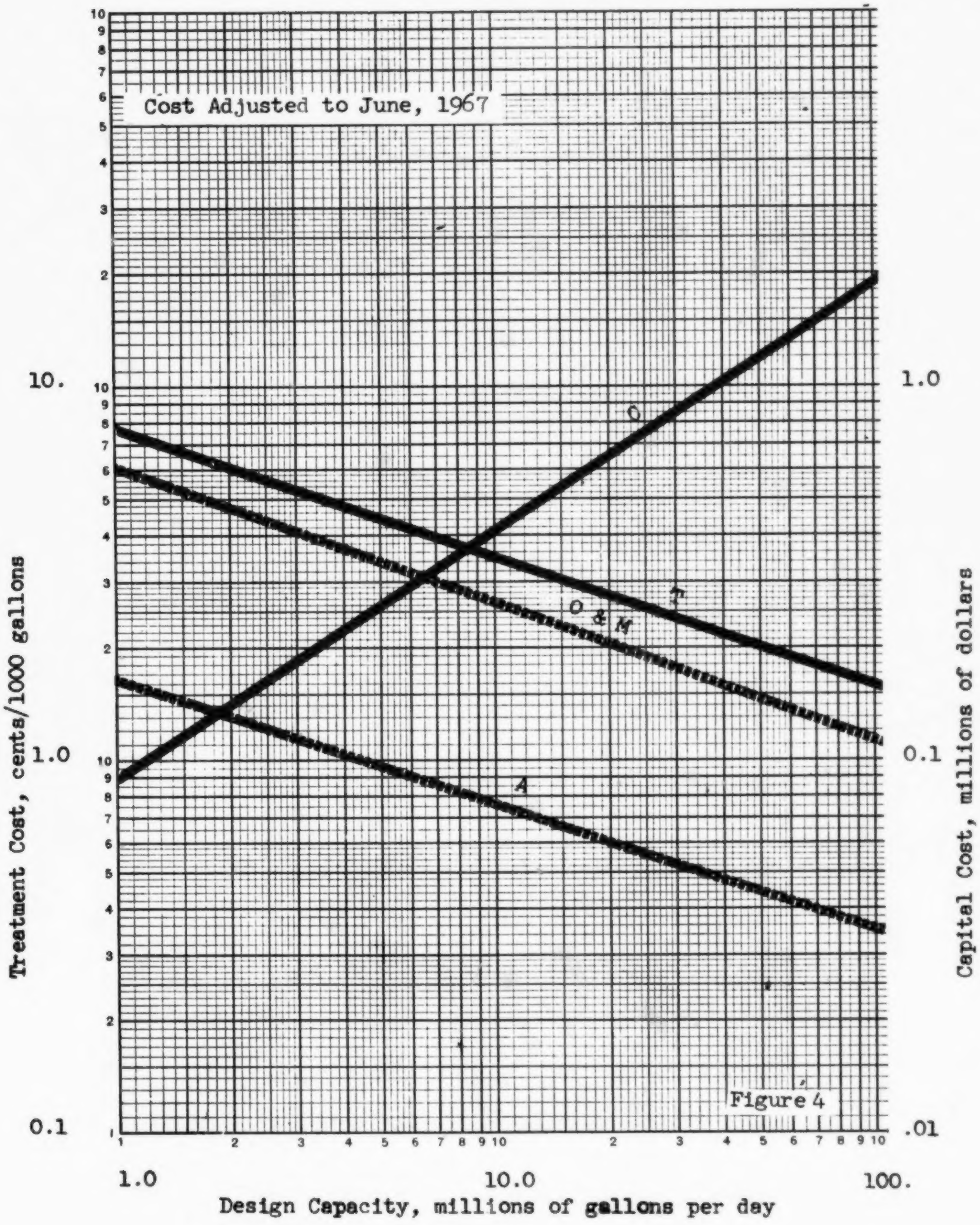
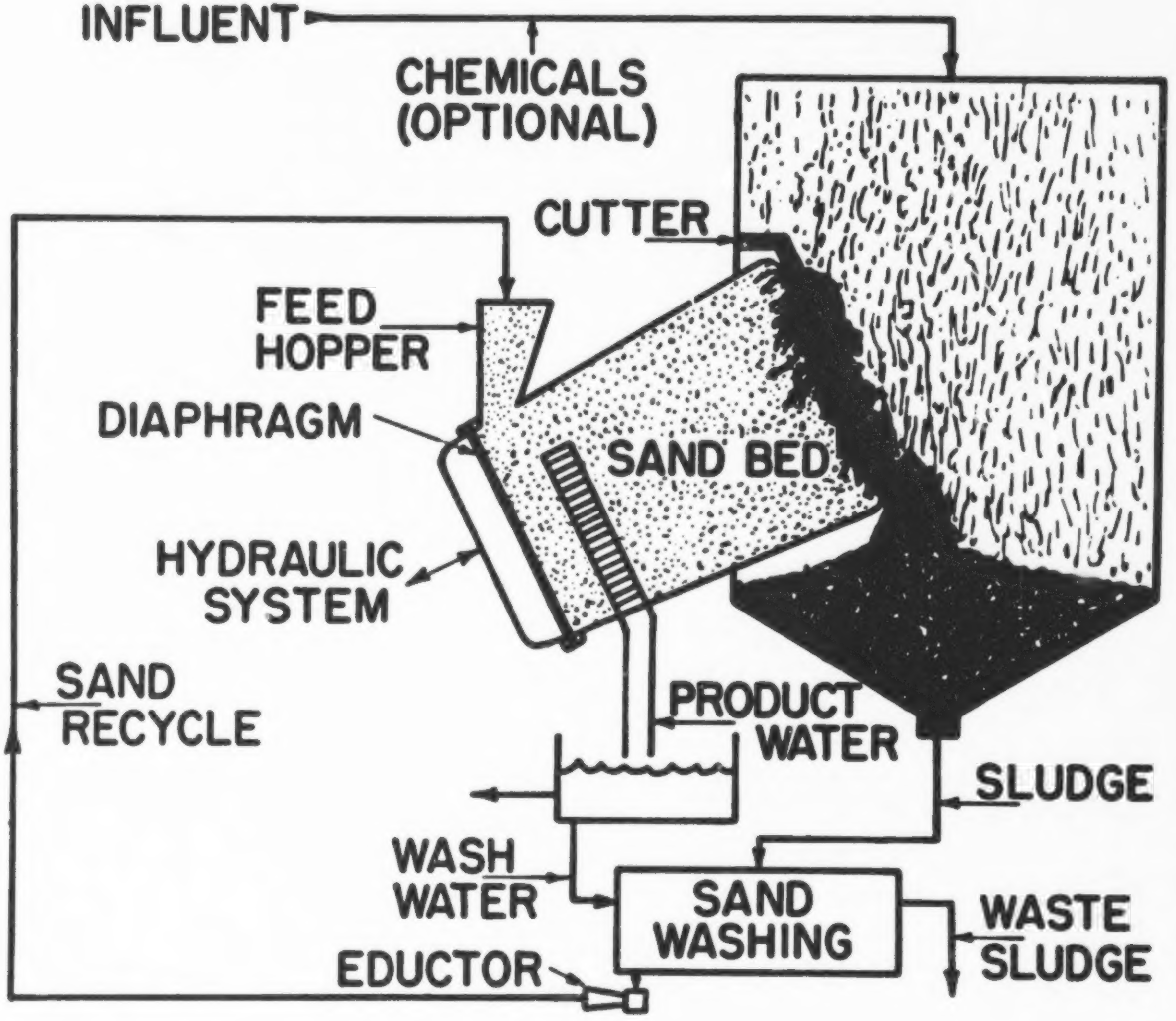


Figure 4

C = Capital Cost, millions of dollars
A = Debt Service, cents per 1000 gallons(4 1/2% - 25 yr.)
O & M = Operating and Maintenance Cost, cents per 1000 gallons
T = Total Treatment Cost, cents per 1000 gallons

BASIC CONCEPT OF MOVING BED FILTER


INFLUENT
CHEMICALS (OPTIONAL)
CUTTER
FEED HOPPER
DIAPHRAGM
SAND BED
HYDRAULIC SYSTEM
SAND RECYCLE
PRODUCT WATER
SLUDGE
WASH WATER
SAND WASHING
WASTE SLUDGE
EDUCTOR

ORGANIC RESIDUE REMOVAL

Arthur N. Masse

I. Introduction

A. At the present time, a limited number of communities have found it necessary to reduce the organic content of their wastewater effluent below the level that can be attained by the conventional biological processes. With the inevitable increase in production and discharge of organic materials (some of which will be resistant to biological degradation) and the inevitable increase in the demand for higher water quality throughout the country, the need for supplementary organic removal processes will become more widespread.

B. The Federal Water Pollution Control Administration and others have been and are conducting research and development projects to meet this need. Adsorption on granular activated carbon has been developed to the point where it is being applied at a scale of 7.5 mgd. Improvements in the economics of the process are still possible, however, and research is being conducted on both the contacting and regeneration phases of the process.

C. Powdered activated carbon is also capable of almost complete removal of organic contaminants from wastewater. The contacting and regeneration processes for powdered carbon are quite different from those used with granular carbon. This process is being evaluated at the 10 gpm level. The economics relative to the granular carbon process are not yet firm.

D. Interest is accelerating in the use of the activated carbon processes, both powdered and granular, as a substitute for the conventional biological processes of municipal waste treatment. Within the next few years, we should know the potential of this application of activated carbon.

E. Chemical oxidation of the organic materials remaining after biological treatment is being studied vigorously. A pilot plant to evaluate the economics of a process using ozone as the oxidant is being planned.

II. Mechanism of Adsorption

A. Adsorption is a phenomenon by which solutes in a solution are attracted to and adhere to the surface of solid materials. Activated carbon is a particularly good adsorbent because it has an extremely large surface area per unit of volume -- areas of 1000 m^2/gm are not uncommon. The bulk of the area is on the walls of pores in the granule. The driving force for adsorption is a function of concentration and type of the material to be adsorbed, the quantity and type of active surface area available and, to a lesser degree, pH and temperature.

B. Various theories have been proposed for the adsorption phenomenon but, in general, the process mechanisms are still largely unexplained. One empirical formula, the Freundlich adsorption isotherm, states that the quantity of material adsorbed per unit weight of adsorbent is proportional to the concentration of solute in equilibrium with the adsorbent. This equation can be written as follows:

$$\frac{X}{M} = kC^{1/n}$$

where X = weight of material adsorbed

M = weight of adsorbent

C = equilibrium concentration of materials remaining unadsorbed in solution

k and n = constants which have different values for each solute and adsorbent. They are also temperature and pH dependent.

This formula does not take into account the fact that the adsorbent will reach a saturation point at which further increases in concentration will not increase the loading.

C. Figure 1 shows isotherm data taken by adding different amounts of carbon to given quantities of wastewater and measuring residual chemical oxygen demands after equilibrium has been reached. With granular carbons, this may take several days so the carbon is pulverized for the test. The lines can be extrapolated to the feed concentrations (C_o) to determine the adsorption capacity of the carbon for the organic material in a given wastewater.

D. Some generalities relating to the type of materials adsorbable by carbon are:

1. The more ionic a material is, the more difficult it is to adsorb.
2. Sparingly soluble materials are generally adsorbed better than highly soluble materials.
3. High-molecular-weight materials may be adsorbed better than those of low molecular weight. There are exceptions: ABS,

for instance, is a very soluble material and yet is adsorbed well on carbon and other adsorbents.

4. In industrial and municipal wastes, mixtures of materials complicate the problem. When adsorption is applied to two materials such as phenol and ABS, each inhibits the other's adsorption. In general, however, the net effect of mixed materials is not detrimental, and there may be an enhancement of the total weight of materials adsorbed from mixtures.

III. The Granular Carbon Process

A. Granular carbons lend themselves well to operation in packed columns. In the size ranges of interest (4x35 mesh to 12x40 mesh), pressure drop is not excessive, some filtration is accomplished and the carbon can be backwashed. The carbons found promising to date are made from coal or lignite.

B. Columns can be designed for pressure or gravity operation.

1. For pressure operation, columns are operated at maximum pressures of 50 psi and therefore are of steel construction. To permit backwashing, which is essential, a freeboard of about 50% of the depth of the carbon is allowed. Incorporation of a surface wash mechanism into the design aids in backwashing. A protective coating to prevent galvanic corrosion is necessary. Several different types of carbon supports for the bottom of the column are in use but the optimum design for this function has not yet been determined.

2. Gravity columns can be of steel or concrete. The underdrain system, surface wash mechanism and backwash provisions are similar to those of a pressure system.

3. All columns must have provisions for removing the carbon for regeneration.

C. Carbon columns have been used to treat primary effluent (where polymers have been used to enhance the primary settling), secondary effluent, sand-filtered secondary effluent and chemically-clarified secondary effluent. There is no indication that a reasonable level of solids in the feed seriously interferes with the adsorption mechanism but more study is needed on this. Unless a highly clarified effluent is needed or the secondary effluent is of poor quality, pretreatment of a secondary effluent is usually not required.

D. The granular carbon must be transferred from the column to a drain bin (or it can be drained en route), to the regeneration furnace, to a quench tank and then back to the column. A continuous screw conveyor has proved satisfactory for transferring the drained carbon to the regeneration furnace. Hydraulic transfer using an ejector has proved effective for transferring to and from the column.

IV. Contacting with Granular Carbon

A. Downflow operation at rates up to 7 gpm/ft^2 in four columns in series has been practiced. Recent economic studies indicate that two-column operation may offer the minimum cost.

B. Packed bed upflow operation allows removal from the bottom of the column of that fraction of the carbon which has become exhausted. Backwashing is difficult with this arrangement and pretreatment of the feed is recommended.

C. Upflow fluid bed operation has been evaluated. This system does not allow the use of a significantly smaller mesh size as had been expected because of the tendency of the smaller particles to be washed out of the column. Pumping costs are less with this system than with the packed beds but the filtration advantage of the packed beds is lost.

D. There is an inverse relationship between the contact time and the rate of regeneration in a granular carbon system. Existing and planned systems allow empty bed contact times ranging from 20 to 40 minutes. Carbon usage rates range between 250 and 400 pounds per million gallons.

V. Granular Carbon Regeneration

A. Thermal regeneration in a multiple hearth furnace is being used in all plants presently treating wastewater with granular carbon.

   1. The drained carbon (40% moisture) is fed into the furnace where it is first dried, the volatiles are then removed and, in the final step, the adsorbed residue is pyrolized. Total residence time in the furnace is about 30 minutes with about 1/3 of this time being at the maximum temperature of 1700°F.

2. Physical losses during the regeneration operation range from 5 to 10% but it is felt that, in a well-designed, continuously-operating system, the losses can be maintained at less than 5%.
3. Table 1 shows the effect of four cycles of exhaustion-regeneration on carbon capacity. Recently-developed improvements in regeneration procedures show promise of improving the recovery of adsorption capacity.
4. Control of air pollution is essential in carbon regeneration. Particulates and odorants must be removed from the furnace stack gases.

B. Chemical regeneration using strong oxidants has been unsuccessful. Regeneration with a strong caustic solution, either as a pretreatment for thermal regeneration or by itself, is being investigated.

C. Several other regeneration techniques are being considered.

1. Electrolysis of a strong saline solution and passage of this solution over the carbon have been proposed.
2. Laboratory studies have indicated that the electric potential of carbon has a significant effect on its adsorption capacity. This technique could have application for desorption, i.e., regeneration.

VI. Applications of Granular Carbon

A. At Lake Tahoe, California, 7.5 mgd of secondary effluent is being lime-clarified, air-stripped, filtered and passed upflow through packed beds of granular carbon. The adsorption part of the operation

Table 1

Effect of Regeneration on Granular Carbon Capacity in the Treatment of Secondary Effluent
Pomona, California

Contactor No.	Regeneration Cycle	Dosage lb Carbon/10^6 gal
II	0	225
	1	315
	2	341
	3	379
III	0	330
	1	327
	2	346
	3	360
IV	0	267
	1	325
	2	35/
	3	349
V	0	274
	1	331
	2	379
	3	-

reduces the COD from 17 to 10 mg/l, the BOD from 4 to 1 mg/l, the color from 20 units to colorless and removes the last trace of odor. The overall process, from raw influent to final product, removes all of the suspended solids, 99.8% of the BOD, 96% of the COD, 98% of the MBAS, 94% of the phosphorous and 50 to 98% of the nitrogen.

B. A 5-mgd plant is being designed for installation at Piscataway, Maryland. Phosphorous will be removed from the secondary effluent by lime precipitation and filtration. The filtered water will be passed downflow over two beds of granular carbon in series.

C. At Pomona, California, 200 gpm of untreated secondary effluent is being passed downflow over four beds of granular carbon in series. The COD is reduced from 35 to 7 mg/l and the suspended solids from 10 to less than 1 mg/l.

D. Nassau County in Long Island is treating 400 gpm of secondary effluent by alum clarification and carbon adsorption. The product will be injected into the ground to prevent sea water intrusion into the groundwater supply.

VII. The Powdered Carbon Process

A. Reduction of the particle size of activated carbon has little effect on the ultimate capacity of the carbon but it does have a dramatic effect on the rate of adsorption. A powdered carbon with a median particle size of 10 microns will come to 90% of equilibrium in less than 10 minutes while a granular carbon may take several days to reach the same state.

B. The powdered carbon process is at a much earlier stage of development than the granular carbon process. Problems in contacting, separation and regeneration are being worked on.

VIII. Contacting with Powdered Carbon

A. Columnar contacting proved impossible because of excessive pressure drop with the finely ground carbon. Mixtures of filter aids with carbon reduced the pressure drop but not enough to make columnar contacting feasible.

B. Slurry contacting in a mixer-settler operation is the presently-recommended procedure for powdered carbon contacting.

1. The carbon dosage required with powdered carbon is several times that required with granular carbon because, in a mixer-settler operation, the carbon is not in equilibrium with the feed (as in a staged granular carbon system) but with a water intermediate in organic concentration between the feed and the product.

2. Powdered carbon dosage is inversely proportional to the number of stages in a mixer-settler system. An infinite number of stages would give the same carbon dosage as a granular system. Preliminary economic studies indicate that two stages provide a minimum cost configuration.

C. A 10 gpm powdered carbon contacting system at our Lebanon, Ohio pilot plant consists of two stages in which the wastewater and the carbon are contacted countercurrently. Each stage consists of three tanks in which we provide rapid mixing, flocculation and sedimentation, respectively. An organic polyelectrolyte is added to each stage to promote floc formation. The product from the final settler is filtered to remove the 10 ppm or so of powdered carbon that cannot be removed by settling.

1. A powdered carbon addition rate of 200 ppm to secondary effluent produces a water with a COD of about 5 ppm and a turbidity of less than 0.5 Jackson Units.
2. Surges in suspended solids content of the feed are easily handled by the powdered carbon process since flocculation and sedimentation are inherent in the process.
3. A spent carbon slurry containing 2-3% solids which can be thickened to 6-8% solids is the waste stream from the process.
4. The process utilizes the conventional unit operations of sanitary engineering, i.e., mixing, flocculation, settling and filtration.

D. Infilco, Incorporated has been operating a 14 gpm two-stage powdered carbon system in which each stage consists of an Accelator unit so that mixing, flocculation and sedimentation occur in one vessel. The units are followed by a sand filter.

1. Using 140 ppm powdered carbon and treating secondary effluent, the product COD is about 7 ppm. The turbidity was less than 1 Jackson Unit.
2. Using only one stage, the carbon dosage required to reach this product quality is 3-4 times that required for two stages.
3. Spent carbon blow-down ranged from 12 to 20% solids.

IX. Powdered Carbon Regeneration

A. Regeneration of powdered carbon has been attempted by the sugar industry but physical losses amounted to 25-30% and little research has been conducted in this field in the last 20 years. The high losses were attributed to agglomeration of the powdered carbon particles during thermal regeneration. This resulted in the formation of "hot spots" and burning of the carbon.

B. Three different types of furnaces for regenerating powdered carbon spent in contact with secondary effluent have been investigated in various laboratories under contract. All three furnaces are designed to maintain the carbon in a finely divided form. Laboratory studies indicated that the carbon could be regenerated successfully and that losses could be controlled to less than 10%. All systems utilize wet scrubbers to recover the carbon from the exit gas stream.

   1. A transport reactor in which a carbon slurry is fed just downstream of a burner compartment was evaluated in the laboratory and is now being studied at the pilot plant scale. The contact time is a matter of a few seconds and the maximum temperature is about 1600°F. Early results have been discouraging because of corrosion and erosion at the point at which carbon is introduced but these problems are gradually being overcome. Recoveries of about 90% of the feed carbon have been obtained.

   2. Another regeneration furnace utilizes a fluidized bed of sand as a heat sink and to keep the carbon in particulate form. This

furnace was designed to be fed a pre-dried carbon. Results in the laboratory were similar to those with the transport reactor but it has not yet been evaluated in the pilot plant.

3. The third type of furnace investigated uses microwave energy to generate heat in a pre-dried carbon. This unit is still in the laboratory stage.

X. Economics of Carbon Adsorption

A. Table 2 shows the most recent cost estimate for adsorption on granular activated carbon in a pressure system. At 10 mgd, this plant will reduce the total COD from 60 mg/l to 7 mg/l. The cost is quite sensitive to capacity. At 1 mgd, the total operating cost will be over 25¢/1000 gallons and at 100 mgd, it will cost about 7¢/1000 gallons. Improvements in contacting and regeneration systems may effect a 25% reduction in these costs at the 10-mgd level.

B. Less is known about the economics of the powdered carbon process. Successful completion of the regeneration studies now underway should make it competitive with granular carbon. There is a potential for significant improvement in the contacting process but the effect of this improvement on economics is not yet known.

XI. Carbon Adsorption as a Substitute for Secondary Treatment

A. A Research and Development Grant has been awarded to the Cuyahoga County Sanitation District for construction and evaluation of a granular carbon system to treat primary effluent. The plant will be designed for a flow of 10 mgd and will be located at Rocky River, Ohio, a Cleveland suburb. Primary treatment will be enhanced by

Table 2

Cost Estimate for 10 mgd Granular Carbon Contacting Plant

Contactor Type	Downflow	Vessel Size	13' ID x 30'
Velocity, gpm/ft^2	7	Carbon Depth	23'
Contact Time, Min.	50	Number of Vessels	18
Particle Size, Mesh	8x30	Number of Trains	8
Regeneration Loss, %	5		
Carbon Capacity, lb COD/lb C	0.522		

Investment, $M

Concrete	126
Adsorbers	385
Tanks	5
Pumps	68
Special Equipment	40
Piping	213
Conveyors	4
TOTAL MAJOR MATERIAL	841
Plant Investment	1,294
Carbon at 26¢/lb	345
FIXED-CAPITAL INVESTMENT	1,639

Operating Costs, ¢/1000 gal.

Make-up carbon at 26¢/lb	1.09
Power at 1¢/kwh	1.01
Backwash water at 6¢/M gal	0.31
Fuel Gas at 25¢/MM Btu	0.15
Labor at $3.50/Man Hour	1.05
Overhead at 50% Labor + 1.485% PI/yr	1.05
Amortization at 7.4% FCI/yr	3.32
Maintenance at 5.75% PI/yr	2.04
Insurance at 1% FCI/yr	0.45
TOTAL OPERATING COST	10.47

the addition of a polymer (or, possibly, a coagulant to remove phosphate) and then the wastewater will be passed over beds of granular carbon. Table 3 shows results obtained in pilot-scale studies at Rocky River.

B. Primary effluent has been fed to the 10-gpm powdered carbon pilot plant at Lebanon. Separation of the carbon and water promises to be more difficult with primary effluent than with secondary effluent. Table 4 shows the product quality obtained. The product was, in most cases, lower in TOC and turbidity than the effluent from the final clarifier of the activated sludge plant.

C. Two contracts are being negotiated for further work on powdered carbon treatment of primary or raw sewage.

   1. Infilco, Incorporated will feed both raw sewage and primary effluent to their two-stage Accelator unit.
   2. In the other proposed contract, raw sewage will be chemically clarified and fed to a two-stage powdered carbon contacting system.
   3. Powdered carbon regeneration will be evaluated at both sites in the later stages of the contract work.

D. Replacement of the biological treatment process by one or more physical-chemical processes is an attractive possibility. The physical-chemical treatment processes should be easier to control, less subject to variations in temperature and toxicity and should

Table 3

Rocky River Waste Treatment Plant
Treatment of Primary Effluent with Granular Activated Carbon

	Raw Sewage	Primary Effluent	Carbon Effluent			
			Empty Bed Contact Time, Min.			
			4.7	14.0	23.4	32.6
Suspended Solids, mg/l	107	65	31	13	15	7
BOD, mg/l	118	57	27	21	11	8
COD, mg/l	235	177	117	67	50	44
TOC, mg/l	52	53	33	18	15	13

Table 4

Powdered Carbon Treatment of Primary Effluent
Lebanon, Ohio

Flow: 5 gpm

Carbon: 200 mg Aqua Nuchar A

Polymer: 1st stage - 1.0 mg/l
2nd stage - 1.5 mg/l

June 13-17, 1967

TOC (ppm)	Feed	Product
High	216.0	32.5
Low	21.0	4.4
Avg.	69.0	10.2

Turbidity (JU)	Feed	Product
High	90.0	10.0
Low	12.5	0.83
Avg.	41.7	3.3

July 11-14, 1967

TOC (ppm)	Feed	Product
High	67.0	5.8
Low	14.6	1.6
Avg.	41.7	3.7

Turbidity (JU)	Feed	Product
High	38.0	2.8
Low	9.0	0.03
Avg.	23.4	1.0

considerably reduce the sludge disposal problem now reaching serious proportions with many plants. The cost of carbon adsorption, when treating primary effluent, should be little, if any, more expensive than when treating secondary effluent.

XII. Oxidation of Residual Organics with Ozone

A. The mechanism of oxidation of organic materials in wastewater is not well understood. One type of reaction that appears to be important is attack by free radicals, especially hydroxyl free radicals, on hydrogen atoms attached to a carbon atom. This mechanism, while it does not directly result in splitting carbon-carbon bonds, may produce intermediate products that can undergo decarboxylation to CO_2. These reactions and, no doubt, many others can result in a decrease in the organic content of wastewater.

B. Countercurrent contacting of wastewater and ozone-oxygen mixtures in a packed column proved an inefficient method of contacting because of the instability of ozone and the low reaction rates between ozone and the organic contaminants. A system of co-current contacts using a high shear injector to promote intimate contact between the gas stream and the water proved more efficient.

C. A 50,000 gpd pilot plant is being considered to further our knowledge of this system. The plant will consist of six co-current contactors in series using high-shear devices for obtaining intimate contact between the ozone-oxygen mixture and the water.

D. Preliminary economic evaluations of ozone contacting indicate that it may be competitive with activated carbon for the treatment of secondary effluent. It is unlikely that ozone can be used to treat primary effluent or raw sewage because the dosage of ozone is linearly related to the organic content of the feed water.

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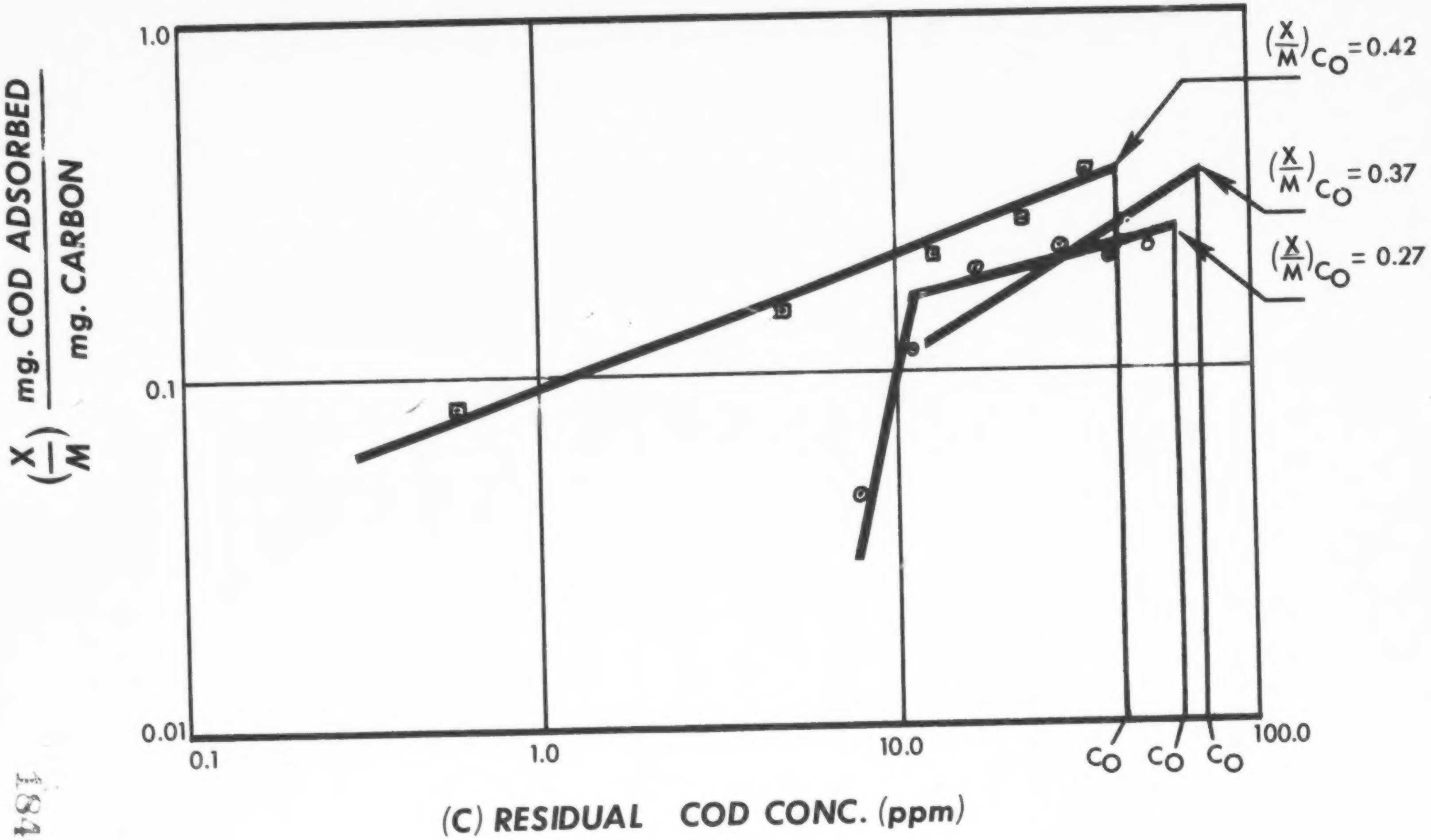
FIGURE 1: COD ISOTHERMS USING VIRGIN CARBON AND DIFFERENT SECONDARY SEWAGE EFFLUENTS



DEMINERALIZATION OF WASTEWATERS

Jesse M. Cohen

I. Introduction

A. Today's best conventional waste treatment processes were not designed to remove non-biologically degradable organics or inorganic salts. It appears certain that improved wastewater treatment will be based on the addition of physical-chemical separation processes to the current biological processes.

B. Degree of treatment required of a renovation process will be determined by the specific purpose for which the water is intended.

C. For certain industrial use and for deliberate municipal recycle, it will be essential to reduce the salt content of wastewater.

D. Need for demineralization is based on the fact that each water-use cycle results in an incremental addition of dissolved inorganic salts.

1. Average values for mineral increments through one municipal use are shown in Figure 1.
2. Increase of total dissolved solids ranges 100-500 mg/1
3. Most important increments, in terms of magnitude, are sodium, sulfate, bicarbonate, and chloride.

E. Three Principal methods are in varying stages of development designed to restore the mineral quality of sewage effluent to at least the quality of river water or better.

1. Electrodialysis
2. Reverse Osmosis
3. Ion Exchange

II. Electrodialysis

Electrodialysis is useful for partial demineralization of low mineralized waters, preferably not exceeding 2000 mg/l of TDS. Since municipal wastewaters generally do not exceed 1000 mg/l, this process is applicable.

A. Principles

1. Principle of operation of an electrodialysis unit is shown in Figure 2. When a direct electric voltage is impressed across a cell containing mineralized water, the positively charged ions (cations) migrate to the negative electrode and the negatively charged ions (anions) migrate to the positive electrode. If cation and anion-permeable membranes are placed alternately between the electrodes, alternate compartments become more concentrated in salts while the intervening compartments become more dilute.
2. Multiple compartments can be interconnected by manifolds which produce two products, one low in dissolved solids, one concentrated. Figure 3.
3. Membranes are composed of ion-exchange materials. The driving force for the migration of ions from solution to the membranes is electrical energy.

B. Operating problems

1. Stagnant films at the membrane surfaces lead to concentration gradients producing scaling from precipitation of compounds with low solubility.

2. Electrolysis of water, which produces hydrogen and hydroxyl ions, leading to increases in power consumption.

3. Deposition of colloidal negatively charged particles on the anion membrane causing fouling and decrease in demineralization.

C. Pilot plant operation

1. Experimental electrodialysis equipment was investigated, Figure 4, with the following conclusions,

2. To maintain operation, the secondary effluent had to be pretreated for removal of organics by activated carbon and clarified by alum coagulation,

3. pH of the concentrate stream was held at 5 or less to prevent calcium carbonate scale formation,

4. Operation was very sensitive to fouling by colloids. Figure 5.

   (a) Extended operation could be maintained only by reducing turbidity to 0.03 JTU. Higher turbidities produced short runs.

   (b) Biological growth on the membranes contributed to fouling.

   (c) Recovery from fouling could be obtained by shutting down for a day or so.

5. Blow-down amounted to about 10% of the product to prevent scaling.

6. Electrodialysis removes ions to varying degrees. Figure 6.

   (a) Selectivity for ions varies with time and with degree of fouling. Both phosphate and sulfate removal rates were affected.

7. Volume of waste concentrate will amount to ≈ 10% of product and methods for disposal of this concentrated waste must be found.

8. Firm costs for electrodialysis are not available. For a 10 mgd plant, capital cost to produce partially demineralized water from wastewater has been estimated at 0.34 dollars per gallon per day and operating costs at 16.1 cents per 1000 gallons. No provision is made in these costs for pretreatment and disposal of brine.

III. Reverse Osmosis

The theoretical capability of reverse osmosis to remove in excess of 90% of the inorganic ions, organic matter and colloids (bacteria and virus) makes this process an important discovery.

A. Principles

1. Figure 7. In normal osmosis when two liquids of differing salt concentrations are separated by a semi-permeable membrane, water will flow from the dilute solution to the more concentrated. Driving force is the concentration gradient.

2. In reverse osmosis pressure, in excess of the osmotic pressure, is applied to the concentrated side causing the normal flow of water to be reversed; i.e., from the concentrated to the dilute side of the membrane.

3. Keys to the successful application of reverse osmosis to wastewater reclamation are:

   (a) Development of a membrane capable of reasonable service under operating conditions,

   (b) Proper incorporation of the membranes into a system to maximize product flow at minimum cost.

B. Membranes

1. Practical reverse osmosis was achieved when Loeb and Sourirajan in 1960 developed a modified cellulose acetate membrane capable of water permeabilities some 500 times greater than earlier films.

2. Membranes consist of two distinct layers. One a spongy porous material which accounts for 99.8% of the thickness and an active layer which accounts for all of the separation of contaminants. Figure 8. Surface layer is typically 0.25μ thick, porous layer 100μ thick.

3. Original theory of operation considered a "straining" mechanism. Current theory is that water molecules dissolve in the membrane material and then diffuse through it. Inorganic ions have lesser solubility in the membrane and have restricted mobility.

C. Water throughput-flux

1. Flux is defined as the flow of water through a membrane, measured in gallons per square foot per day.

2. Flux is directly proportional to applied pressure - minus the osmotic pressure - and inversely proportional to thickness of membrane.

3. Relationship of pressure and salt rejection (solute retention) are shown in Figure 9.

(a) At low pressures, low flows and little salt removals are obtained,

(b) As pressure exceeds osmotic pressure, flow and salt rejection increase and 100% salt rejection is approached asymptotically.

4. Fluxes in the range of 20-40 gfd are required to make RO economically attractive. Current fluxes of ≈10 gfd at 750 psi are common.

5. A major current problem is the inability to maintain flux because of fouling and chemical and physical changes that occur in the membrane.

D. Materials rejected

1. Inorganic salts are rejected in amounts exceeding 90%.

2. Organic molecules, with the exception of certain low molecular weight materials like amines, alcohols and acids, are removed.

3. Suspended and colloidal materials including bacteria, virus and sewage colloids are completely removed.

E. Membrane Separator design

A key factor in practical operation of RO is the mechanical design of the unit.

1. Plate and frame, using flat membrane sheets in a device similar to a filter press was one of the earliest designs. Figure 10.

(a) Units capable of producing 100,000 gal/day have been developed by Aerojet-General. Largely used for brackish water treatment.

2. A simple tubular design consists of porous tubes which are lined with cellulose acetate membranes. Design is similar to heat exchangers. Flow is from inside the tubes at pressure and discharged from the outside surfaces of the tubes at ambient pressure. Figure 11.

3. To obtain a maximum of membrane area in a small volume, a "spiral-wound" design was developed by General Atomics. Several hundred feet of membrane can be accommodated in a cubic foot of pressure vessel volume. Figure 12.

4. The ultimate in greatest area per unit volume is approached by "hollow-fiber" design.

   (a) About 20 million hollow fibers can be packed into a shell 1 foot in diameter and 7 feet long.

   (b) A 12-inch permeater 7 feet long contained in a unit only 5.5 cu.ft. in volume provides about 50,000 square feet of membrane surface and will produce 7500 gal/day.

   (c) Flux with these fibers is small - currently about 0.15 gal/ft^2/day. Fluxes of 1.5 gfd may be attainable but this will still be 1/10 that obtainable with other designs.

   (d) This configuration can be characterized as "very high surface area, low flux permeater."

F. Cost

Application of RO to wastewater is still in early stage of development.

1. Based on experience in treating brackish water, cost estimates have ranged from 30-60 cents/1000 gallons.

2. These problems remain to be solved before RO can be successfully applied to wastewater.

   (a) Increased fluxes

   (b) Maintenance of flux in the face of fouling and physical and chemical changes occurring at the membrane.

(c) Increased product to waste ratios. Up to 90% has been obtained.

(d) Disposal of concentrate

IV. Ion Exchange

Ion exchange has been used for many years in water treatment for softening and boiler water conditioning. Development of newer types of resins which are not fouled by organics and newer techniques of using these resins demonstrate that ion exchange is a practical method for demineralization of wastewater.

A. Principle

1. Ion exchange materials, both natural and synthetic, are absorbents which carry charged ionic groups. To maintain electroneutrality, each ionic site must have associated with it an ion of opposite charge (counter-ion). The success of ion exchange depends on the ability of the counter-ion to be replaced or exchanged for another ion of the same charge.
2. When all counter-ions have been replaced, the ion exchange material is exhausted. Regeneration is obtained by contacting the exchanger with a concentrated solution of the original counter-ion.

B. Classification

1. Ion exchangers are classified by the charge of the exchangeable ion. Thus acid or cationic resins will exchange cations like Ca^{++} and Mg^{++} and base or anionic resins will exchange OH^- or Cl^- anions.

2. Classification also considers the degree of dissociability of the active group. Thus:

    (a) Strong acid resins (cationic) contain sulfonic acid groups

    (b) Weak acid resins (cationic) contain carboxyl or phenolic groups

    (c) Strong base resins (anionic) carry quaternary ammonium groups

    (d) Weak base resins (anionic) usually have amine groups which are only slightly ionized in the OH form.

3. A common matrix material of synthetic resins is styrene or vinyl benzene which has been polymerized and which have ranging functional groups attached. Figure 13.

    (a) A very wide variety of resins can be prepared to meet specific needs by varying functional groups, degree of ionization, and physical characteristics.

C. Selectivity

1. A general purpose resin will exchange any of the common ions but, in a mixture of ions, selectivity will occur

    (a) For strong cation exchangers the order of selectivity is $Ca^{++} < K^{+} < NH_4^{+} < Na^{+}$

    (b) For weak anion exchangers the order of selectivity is $SO_4^{=} < HPO_4^{=} < NO_3^{-} < Cl^{-}$

D. Wastewater demineralization

For demineralization, both an anion and cation exchanger is required, consisting of a weak anion and a strong or weak cation exchanger.

1. For economic demineralization, these requirements for the process must be met.

    (a) Capability of regeneration at theoretical efficiencies using low cost acids and bases

    (b) high operating exchange capacities

    (c) ease of removal of regeneration chemicals with a minimum of rinse water

    (d) Long life of resin to physical and chemical attrition

    (e) Waste regenerants should pose a minimum disposal problem.

E. Desal process developed by Rohm and Haas has promise for economic demineralization of wastewater.

1. One modification consists of a 3-bed design consisting of a weak anion, a weak cation and a weak anion exchanger in series. Figure 14.

    (a) First column converts all anions to the bicarbonate form. Removes all other anions.

    (b) Second column converts bicarbonates to CO_2 and removes cations.

    (c) Third column in OH^- form absorbs CO_2 to become the bicarbonate form. This column then becomes the first in the series after columns 1 and 2 have been regenerated with ammonium hydroxide and sulfuric acid respectively.

2. A modification more applicable to wastewater treatment is shown in Figure 15.

    (a) Weak anion exchanger, in the bicarbonate form, removes all anions: SO_4^{2}, $PO_4^{=}$, NO_3 and Cl^-.

(b) Column effluent is polymer flocculated, CO_2 removed and lime softened which removes: suspended solids, Ca^{++}, Mg^{++} and Fe^{+++}.

(c) Final column, a weak cation exchanger, removes remaining cations: NH_4^+, Na^+ and K^+.

(d) Exchangers regenerated with ammonium hydroxide and sulfuric acid. Calcining of lime would provide CO_2 for conversion of anion exchanger to bicarbonate form.

(e) About one-half of the COD is removed by the anion exchanger and quantitatively removed by the regenerant.

(f) Final product, containing residual amounts of inorganic solids - $\approx$ 50 ppm - and 1/2 of the original COD, could be blended with undemineralized water to reduce cost.

F. Cost

Process has not been applied on a sufficiently large scale to obtain reliable cost data.

1. Estimate for 1 and 10 mgd plants, including capitalization, equipment and chemical costs for the modified Desal process is 17-18 cents/1000 gallon.

(a) CO_2 is assumed to be available

(b) resin life estimated to 3 years

(c) no costs included for ammonium recovery and brine disposal.

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FIG. 1

AVERAGE COMPONENTS IN DOMESTIC SEWAGE EFFLUENTS

CONSTITUENT	APPROX BUILD-UP THROUGH ONE MUN USE	NORMAL RANGE OF BUILD-UP	REPRESENTATIVE SECONDARY EFFLUENT
Ca ($CaCO_3$)	30 ppm	15- 40	95
Mg ($CaCO_3$)	13	20-40	39
Na	55	40-700	84
SO_4	25	10-40	51
CL	35	20-125	50
PO_4	30	15-40	30
NO_3	8	0- 18	8
SiO_2	15	10-20	35
ABS	3	1- 4	3
COD	70	40- 40	70
BOD	15	9- 40	15
TDS	250	100-500	550
HCO_3	65	---	170
pH	---	---	7.5

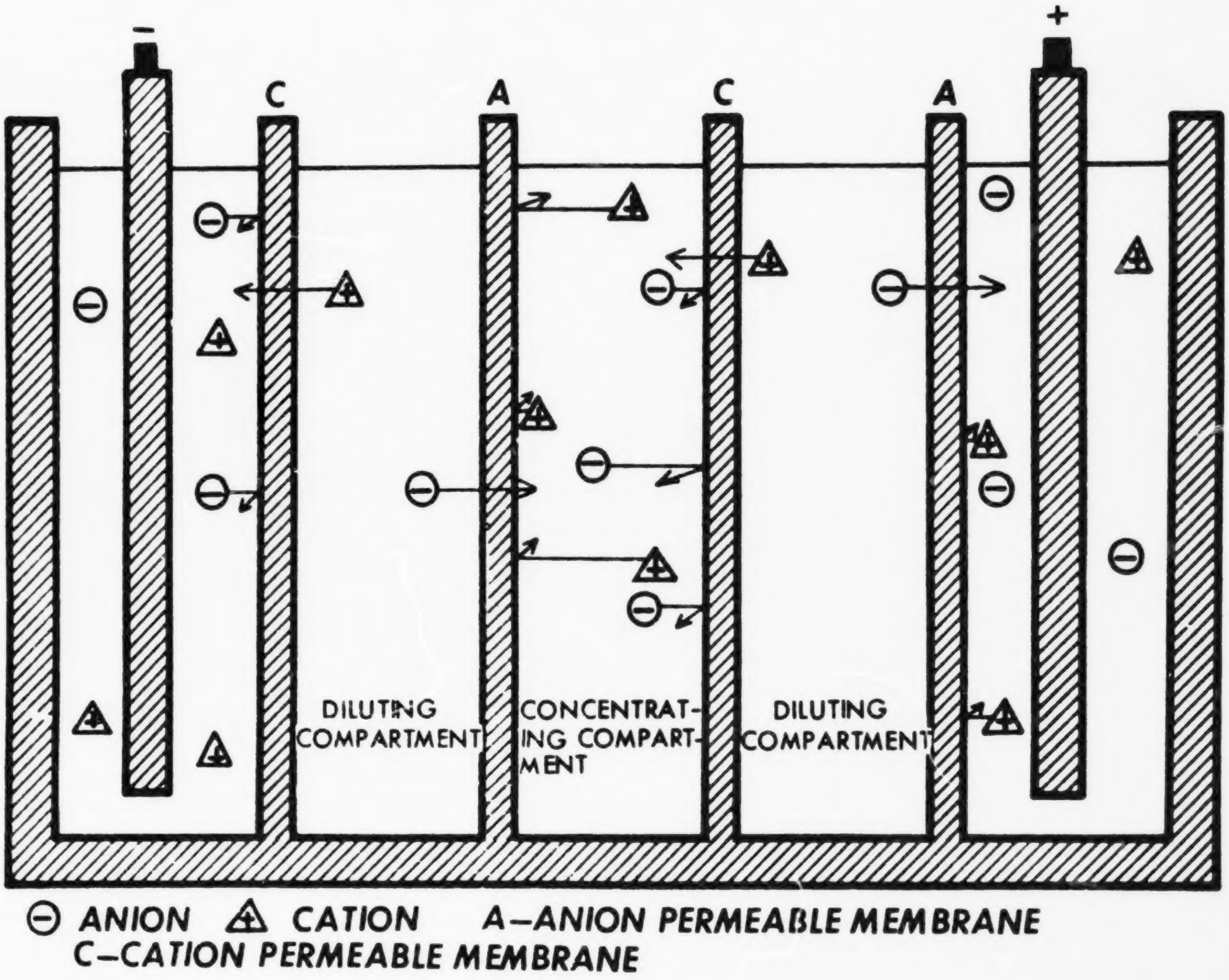

−
+
C
A
C
A
DILUTING COMPARTMENT
CONCENTRATING COMPARTMENT
DILUTING COMPARTMENT
⊖ ANION
△ CATION
A—ANION PERMEABLE MEMBRANE
C—CATION PERMEABLE MEMBRANE

FIGURE 3. ELECTRODIALYSIS PRINCIPLE

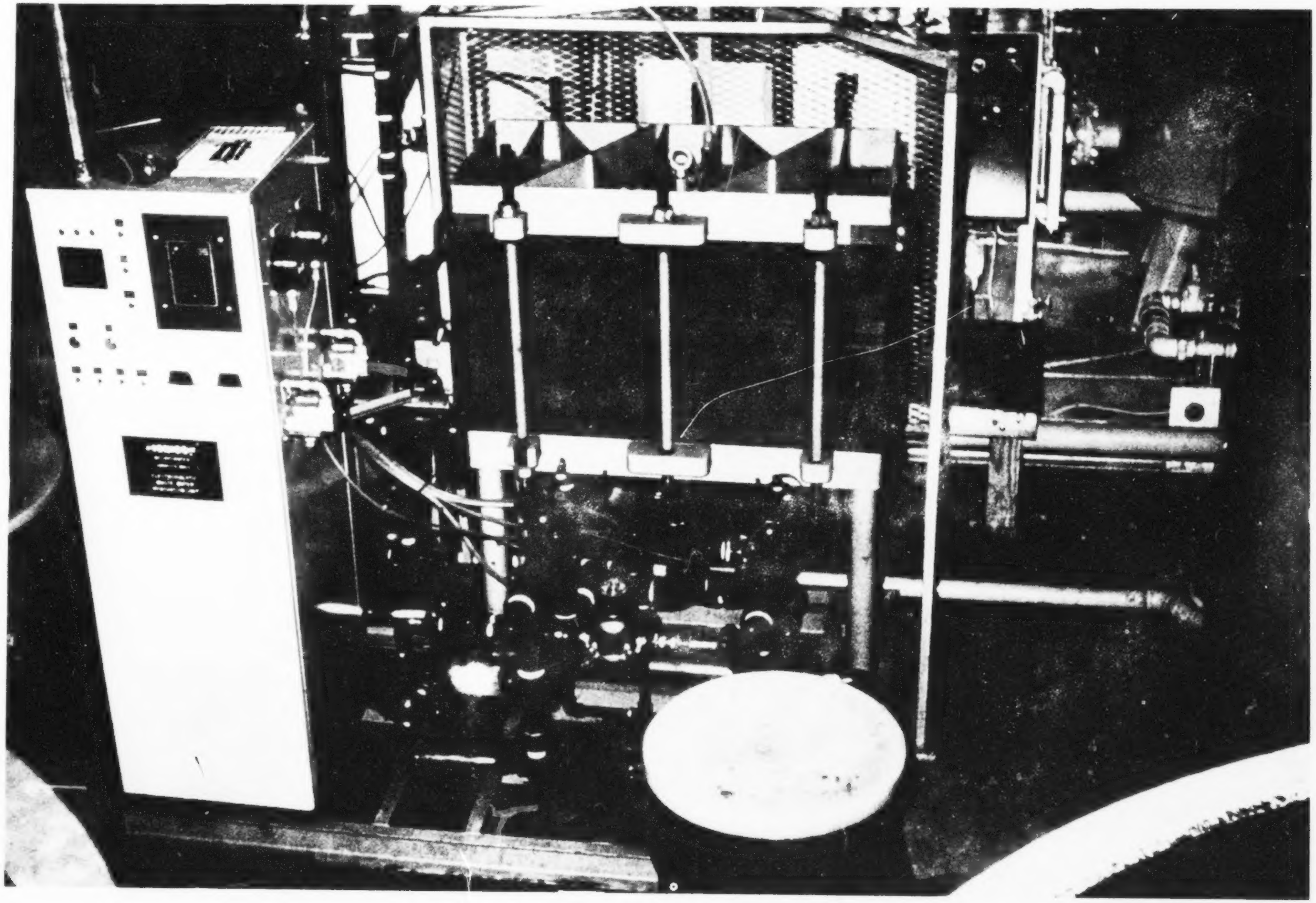


FIG. 4

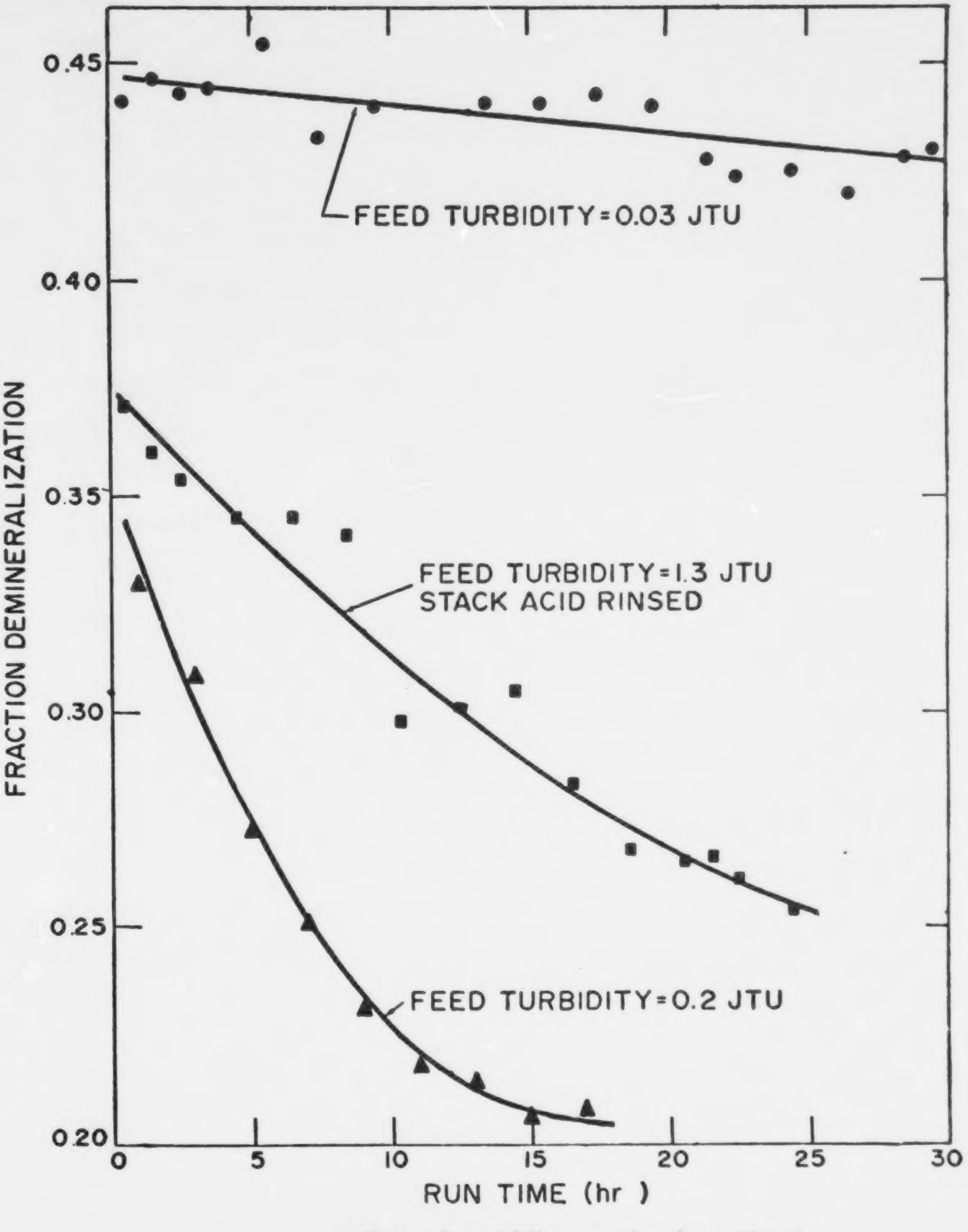


FIG. 5 **Effect of turbidity on demineralization.**

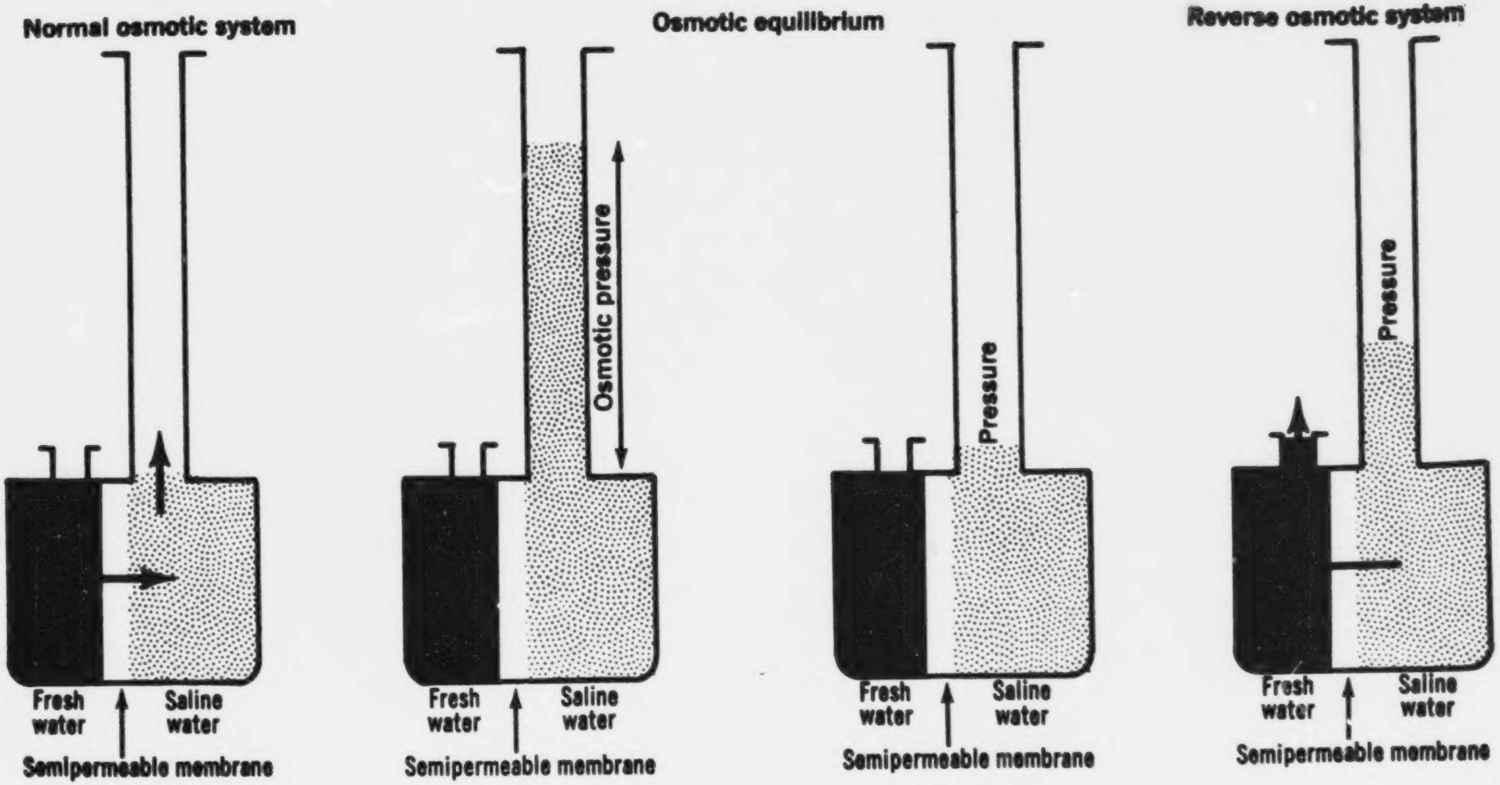
FIG. 6

Ion Removal Selectivity

Ion	Fraction of Ion Removed / Fraction of All Ions Removed	
	Average	Range
Bicarbonate	0.77	0.63–0.95
Chloride	1.25	1.07–1.51
Nitrate	1.22	1.02–1.48
Phosphate	0.72	0.25–1.03
Sulfate	1.11	0.21–2.00
Ammonium	1.15	1.05–1.3
Calcium	1.25	1.01–1.48
Magnesium	0.98	0.71–1.35
Potassium	1.14	0.77–1.35
Sodium	0.79	0.52–0.99
Calcium and magnesium	1.13	1.05–1.28

FIG. 7

Pressure on osmotic system leads to reverse osmosis


Normal osmotic system
Fresh water
Saline water
Semipermeable membrane
Osmotic pressure
Fresh water
Saline water
Semipermeable membrane
Osmotic equilibrium
Pressure
Fresh water
Saline water
Semipermeable membrane
Reverse osmotic system
Pressure
Fresh water
Saline water
Semipermeable membrane

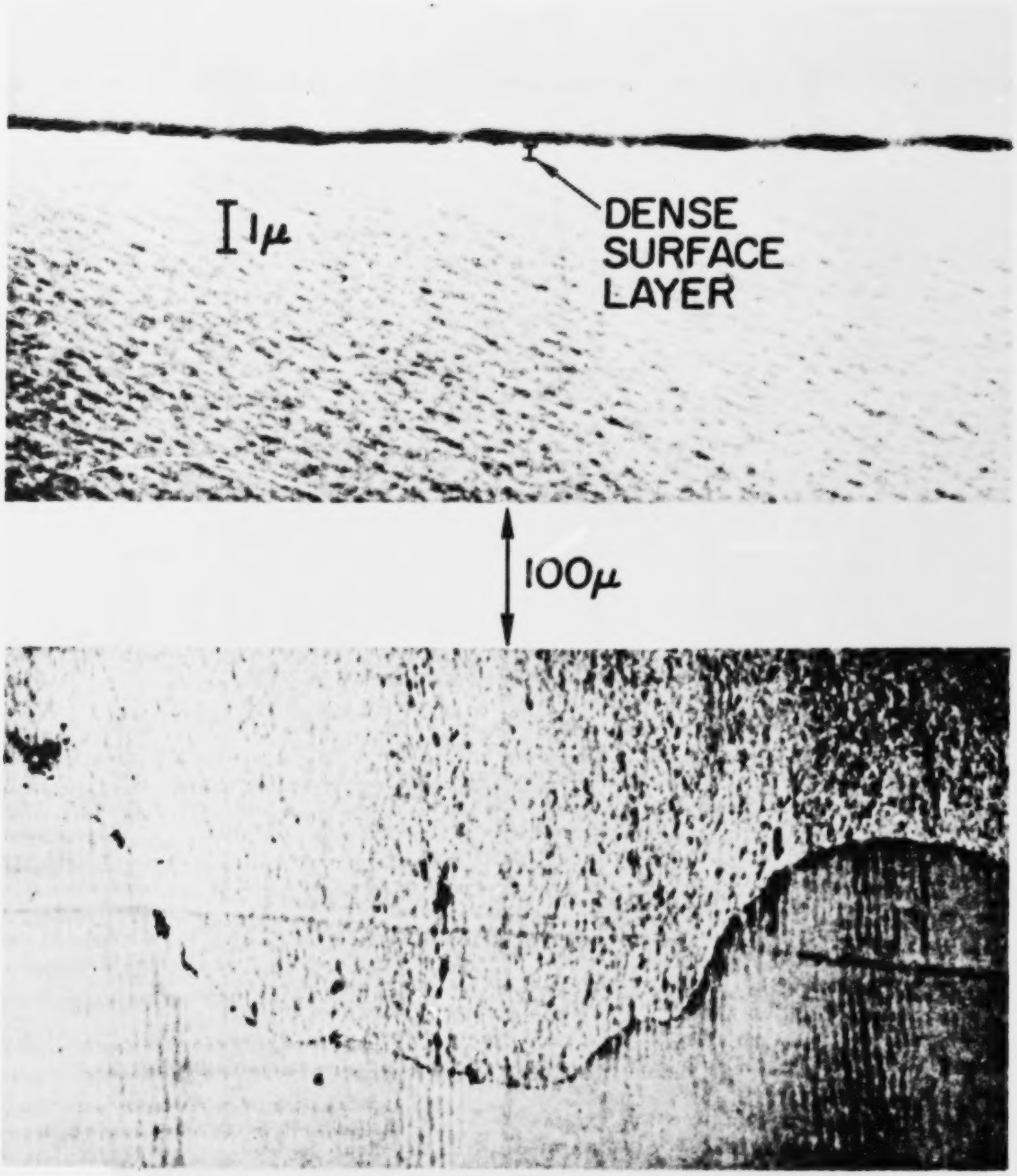

I 1μ
DENSE
SURFACE
LAYER
100μ

FIG. 8

COMPOSITE OF TWO ELECTRON PHOTO-MICROGRAPHS OF CROSS SECTIONS OF MODIFIED CELLULOSE ACETATE MEMBRANE

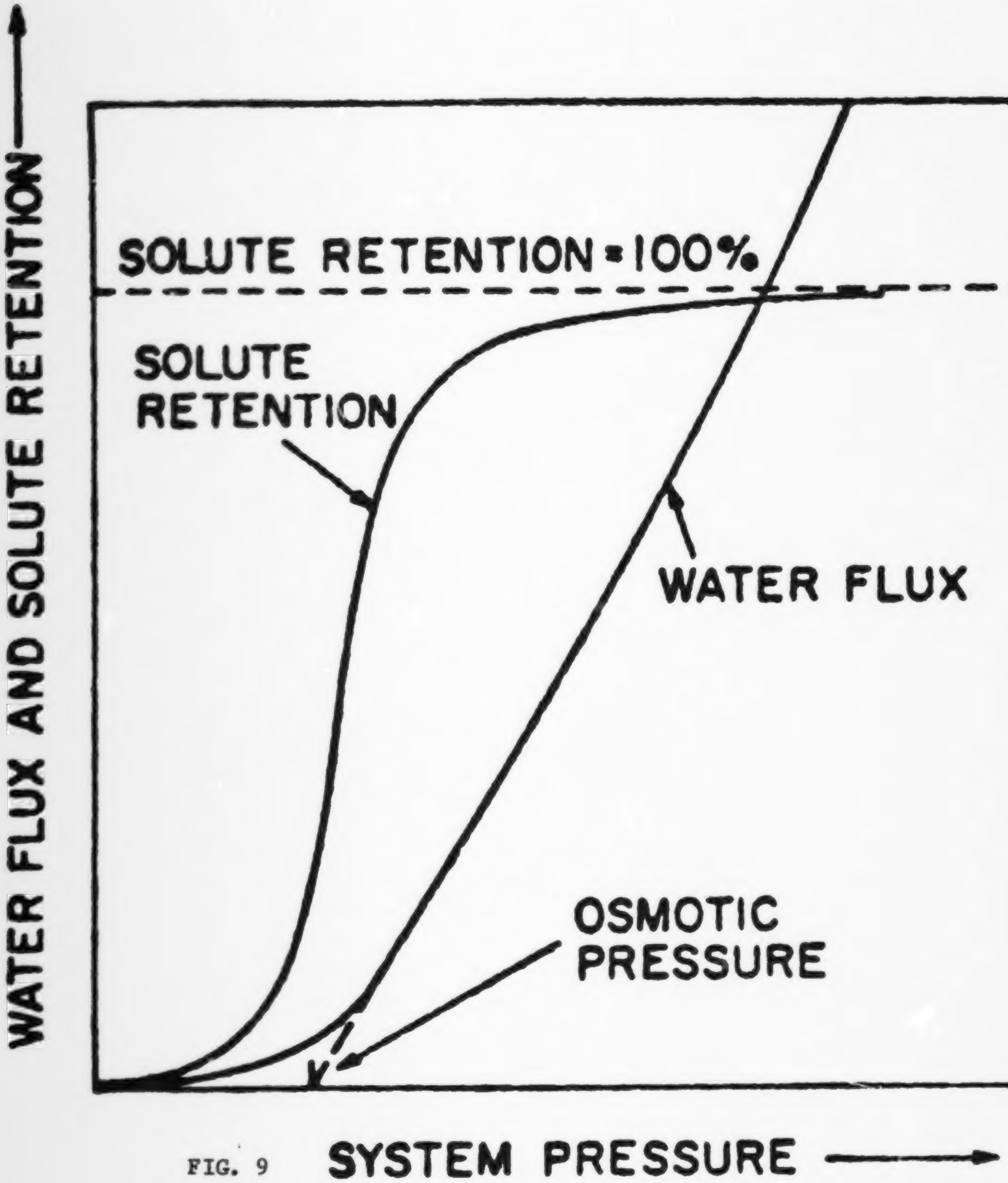
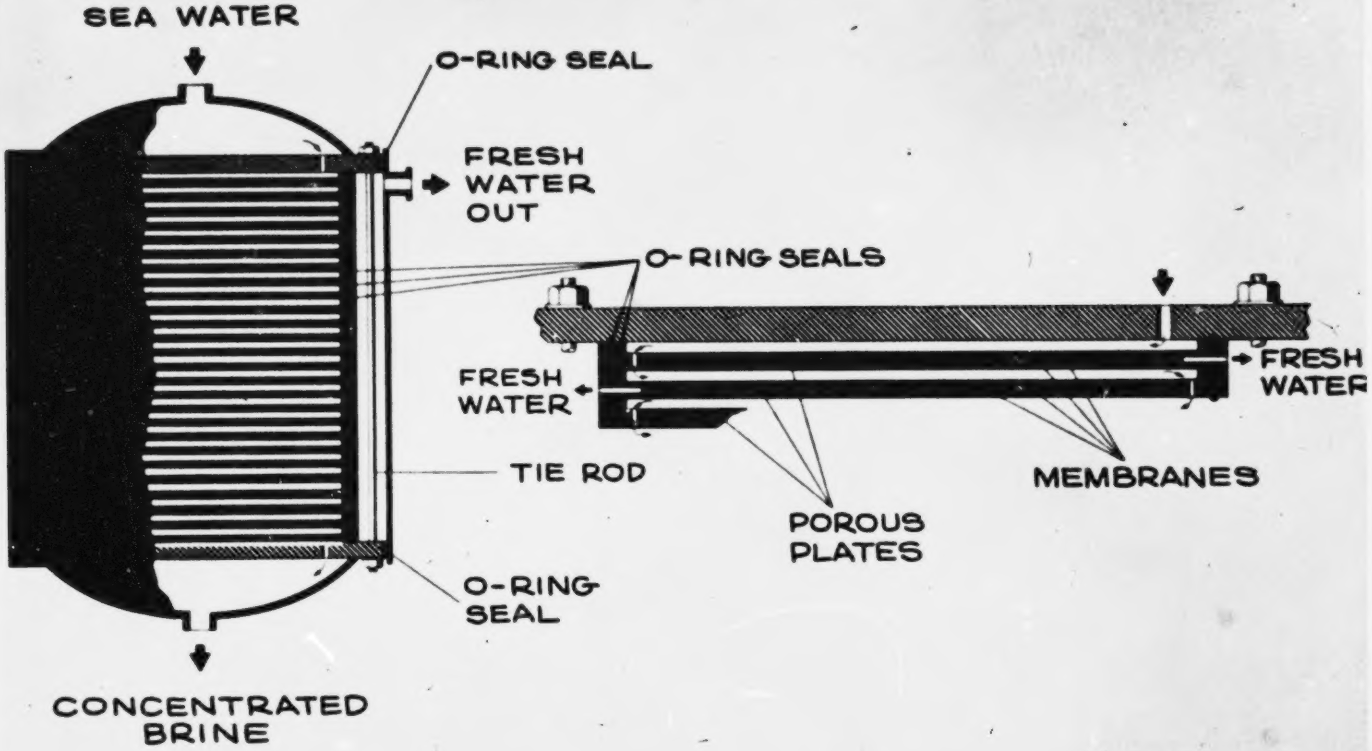


FIG. 9

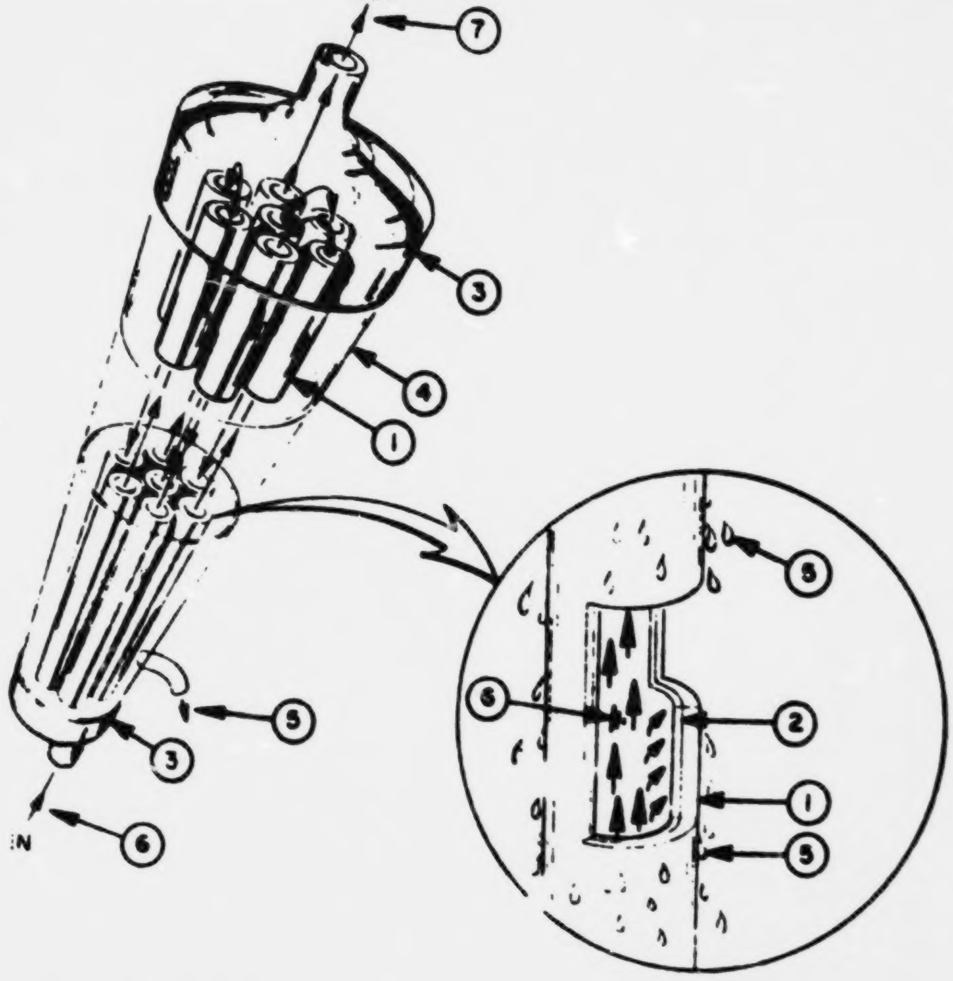
Solute retention and water flux in idealized membrane.

MULTIPLE PLATE TYPE DESALINATION CELL


SEA WATER
O-RING SEAL
FRESH WATER OUT
O-RING SEALS
FRESH WATER
FRESH WATER
TIE ROD
MEMBRANES
POROUS PLATES
O-RING SEAL
CONCENTRATED BRINE

CHEMICAL PRODUCTS DIVISION · VON KARMAN CENTER

FIG. 10


OUT
7
3
4
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3
6
IN
5
6
2
1
5

(1) FIBERGLASS TUBE
(2) OSMOTIC MEMBRANE
(3) END FITTING
(4) PVC SHROUD
to collect product water
(5) PRODUCT WATER
(6) FEED SOLUTION
(7) EFFLUENT

Figure 11 A Tubular Reverse Osmosis Unit

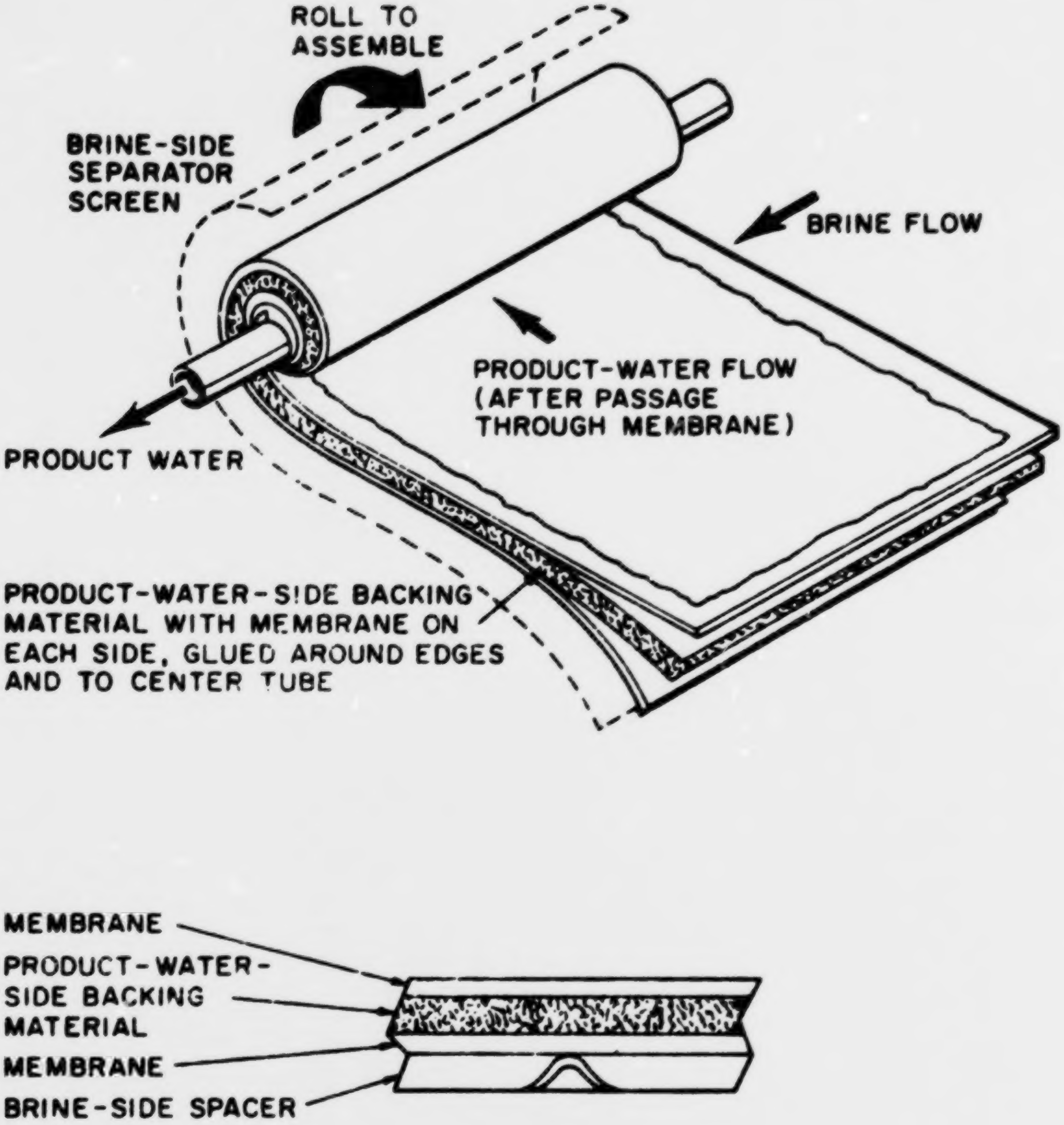
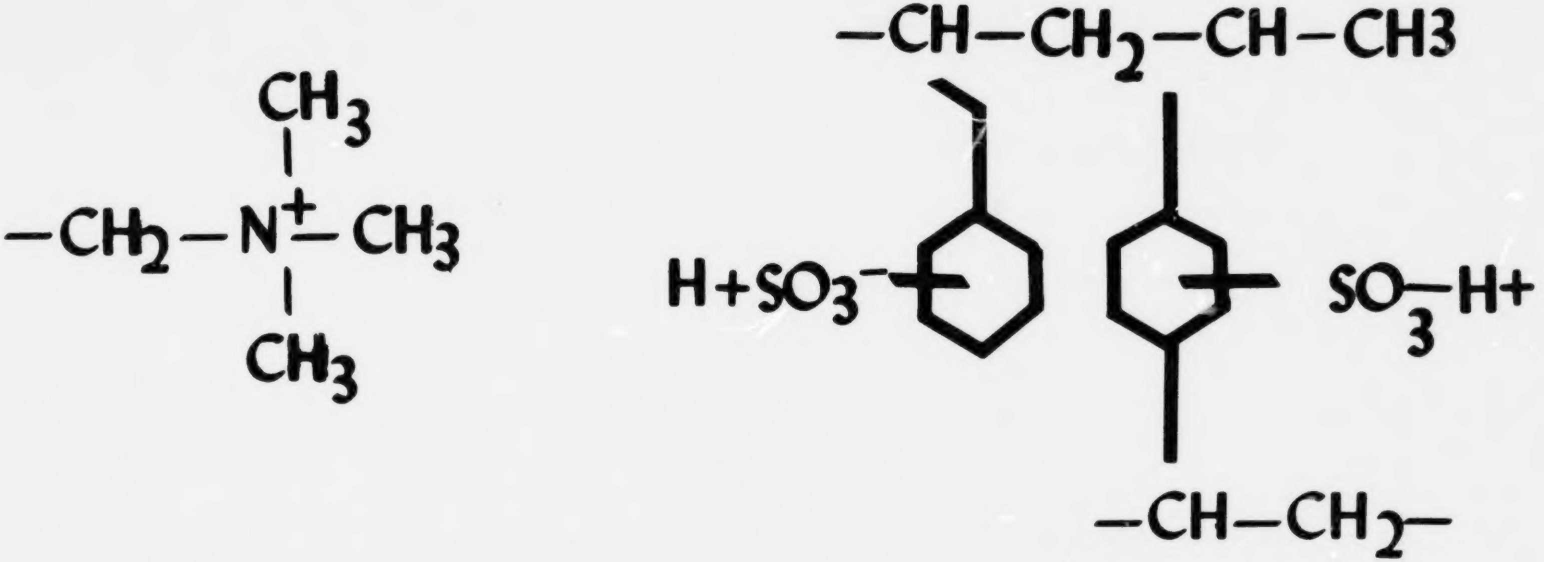

ROLL TO ASSEMBLE
BRINE-SIDE SEPARATOR SCREEN
BRINE FLOW
PRODUCT-WATER FLOW (AFTER PASSAGE THROUGH MEMBRANE)
PRODUCT WATER
PRODUCT-WATER-SIDE BACKING MATERIAL WITH MEMBRANE ON EACH SIDE, GLUED AROUND EDGES AND TO CENTER TUBE
MEMBRANE
PRODUCT-WATER-SIDE BACKING MATERIAL
MEMBRANE
BRINE-SIDE SPACER

Figure 12. A Spiral-Wound Reverse Osmosis Module

Reprinted with permission from General Dynamics, General Atomic Division


CH3
—CH2—N+—CH3
CH3
—CH—CH2—CH—CH3
H+SO3−
SO3—H+
—CH—CH2—

STRONG BASE RESIN

STRONG ACID RESIN

FIG. 13

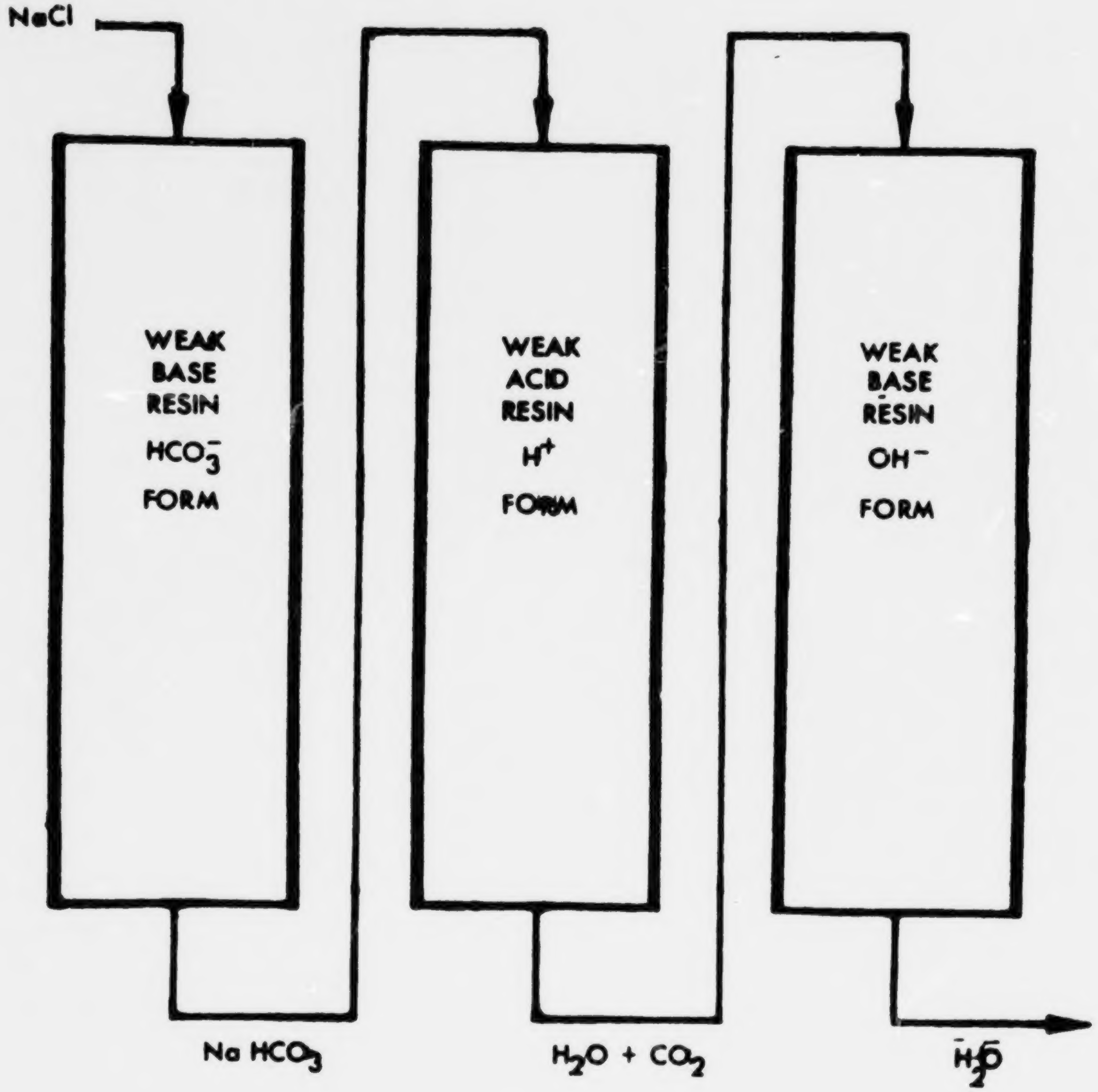

NaCl
WEAK
BASE
RESIN
HCO_3^-
FORM
WEAK
ACID
RESIN
H^+
FORM
WEAK
BASE
RESIN
OH^-
FORM
Na HCO_3
$H_2O + CO_2$
H_2O

Fig.14 **DESAL Process**

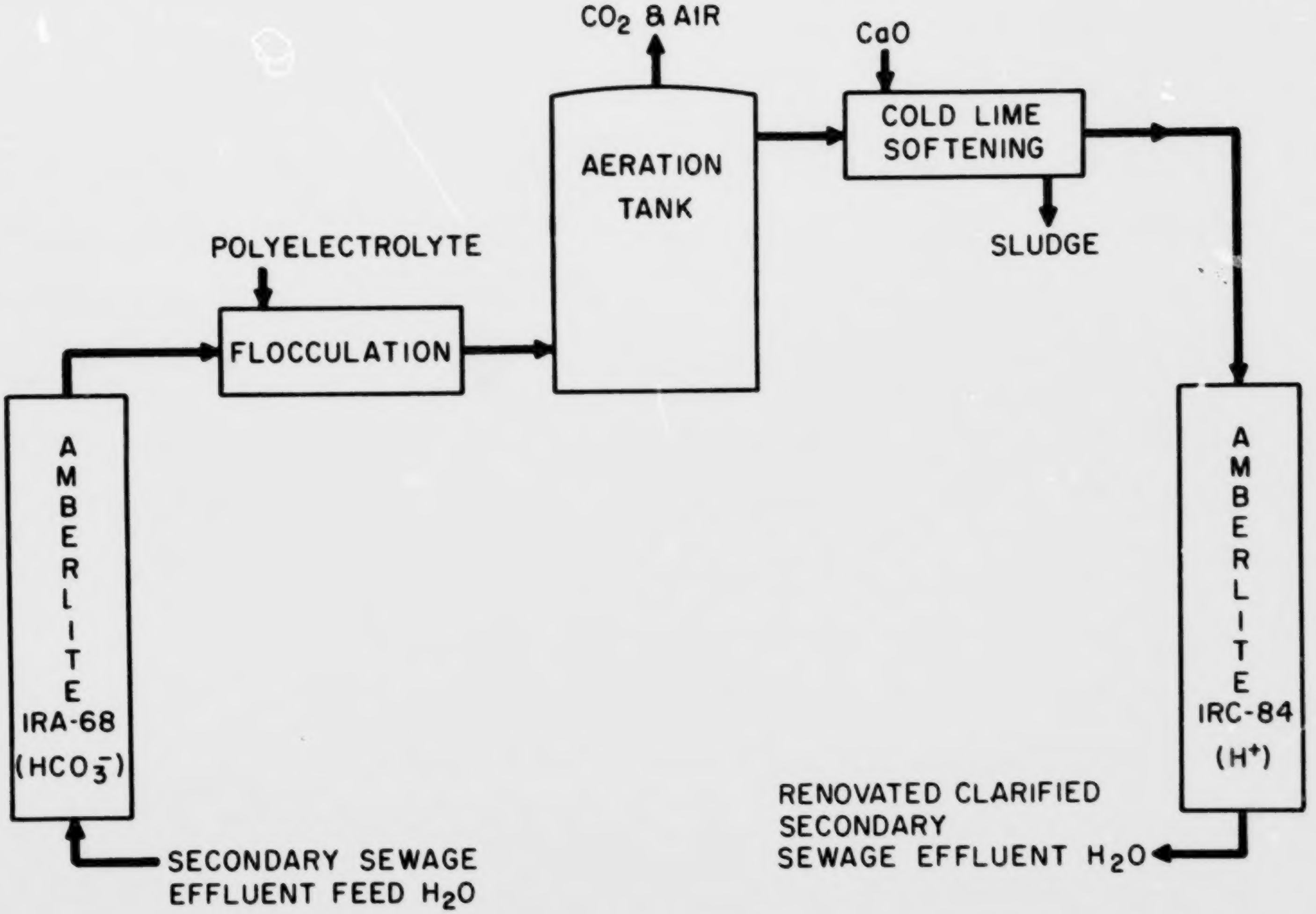

CO$_2$ & AIR
CaO
COLD LIME SOFTENING
AERATION TANK
SLUDGE
POLYELECTROLYTE
FLOCCULATION
AMBERLITE IRA-68 (HCO$_3^-$)
AMBERLITE IRC-84 (H$^+$)
RENOVATED CLARIFIED SECONDARY SEWAGE EFFLUENT H$_2$O
SECONDARY SEWAGE EFFLUENT FEED H$_2$O

Figure 15 Flow diagram of ion exchange process for renovation of secondary sewage effluent

Figure 16 Cost Estimate for Renovation of Haddonfield, N. J., Secondary Sewage Effluent

	$ Cost/1000 Gal.	
	1,000,000 gal./day	10,000,000 gal./day
Alkalization	0.0655	0.0631
Dealkalization	0.0500	0.0478
Carbonation	0.0030	0.0030
Degasification	0.0042	0.0029
Flocculation (chemicals only)	0.0436	0.0436
Lime softening	0.0158	0.0158
Grand total	$0.1821	$0.1762

FOURTH TECHNICAL SESSION

Ralph C. Pickard, Moderator

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NEW DEVELOPMENTS IN SLUDGE HANDLING AND DISPOSAL

Robert B. Dean

I. INTRODUCTION

A. Pollutants removed from wastewaters must be treated in such a way that they will not pollute the environment

1. Only three places to put polluting substances. Air, land, ocean. Not in surface waters.

B. Ocean Disposal

1. Ocean can oxidize wastes if kept aerobic.

    a. Grease should be removed by aerobic treatment.

2. Food chains may concentrate poisons killing larger species.

C. Land Disposal. Fill.

1. Not suitable for soluble substances such as salts.
2. Needs dewatering to produce solid that will bear a load. Useful for insoluble inorganic wastes.

D. Land Disposal. Surface.

1. Not suitable for solubles except nutrients in quantities utilized by plants.
2. Low cost dewatering; can handle liquid sludges.
3. Low cost oxidation of organic matter.

E. Disposal into Wells

1. Unsuitable if there is a chance that pollutants will reach useful ground water or cause earthquakes.

II. ORGANIC SUBSTANCES

A. Principal problem in disposal of organic sludges is water. Twenty to fifty times as much water as all other substances in waste.

1. Oxidation of 1 lb. of organic sludges is sufficient to evaporate about 2 lb. of water.

2. Economics of incineration are therefore closely tied to dewatering by sedimentation, filtration and drying.

B. Treatment of wet sludge to aid further processing

1. Anaerobic digestion. Reduces solids about 50% by hydrolysis and fermentation to methane gas which is burned to CO_2 and water. Produces foul supernatant liquor which returns organics and nutrients to the plant for recycle.
2. Sludge cooking at 370°F. Improves filterability of solids. Returns 10-20% of the BOD and 60-80% of the nitrogen.
3. Wet oxidation - Zimpro at 350°F removes 15% of COD by oxidation; dissolves 25% of solids and 90% of nitrogen. Higher temperatures destroy more solids. Improves filtration, produces a foul supernatant liquor.
4. Aerobic Stabilization.

   a. Stabilizes solids, oxidizes oil and grease, retains nutrients.
   b. Can reduce nitrogen levels by nitrification-denitrification.
   c. Does not aid dewatering.

C. Oxidation and dewatering on land surfaces. An "old-fashioned" process.

1. Low cost dewatering on land.
2. Ammonia, phosphate and pesticides fixed on soil minerals.
3. Soil organisms destroy pollutants.

   a. Organics go to CO_2.
   b. Ammonia converted to nitrates.

4. Soil improved for agriculture and forestry.

III. CHEMICAL SLUDGES

A. Lime

1. $CaCO_3$, $Ca_5OH(PO_4)_3$, $Mg(OH)_2$, $CaSO_4$, $Ca(OH)_2$ Dewater in lagoon or vacuum filter.
2. Land fill
    - a. Alkaline due to excess $Ca(OH)_2$
    - b. Non-leachable $PO_4^{\equiv}$
    - c. $SO_4^{=}$ leaches out, 1300 mg/l
3. Recovery of CaO from $CaCO_3$ by burning.

B. Iron

1. $Fe(OH)_3$, $Fe^{+2} \cdot 2\,Fe^{+3}(OH)_8$, $FePO_4$, $CaCO_3$, $CaSO_4$ -- Dewatering more difficult.
2. Land fill.
3. Iron recovery rarely worthwhile.

C. Aluminum

1. $Al(OH)_3$, $Al\ PO_4$, $CaCO_3$.
2. Very difficult to dewater; Freezing.
3. Aluminate recovery may be practical.

IV. SPECIAL DEWATERING TECHNIQUES

A. Freezing -- Destroys colloidal structure; gives good filtration

1. Needs slow freezing over several hours after thawing.
2. Complete freezing and minimal mechanical agitation.
3. Most promise for Activated Sludge and Aluminum Hydroxide.
4. Does not increase strength of filtrate.
5. Does not kill organisms.

B. Radiation

1. Selectively attacks high polymers and may reduce water holding capacity.
2. Does not disinfect. May kill 90% of microorganisms.
3. Releases organics to filtrate.
4. Requires costly shielding.

C. Pressure Cooking -- 250° C (480° F)

1. Gives good filterability.
2. Strong "soup" needs further treatment.
3. Disinfects.

D. Cooking with SO_2 catalyst

1. Good filterability at lower temperatures and pressures.
2. Strong "soup" may have food value for livestock.
3. Disinfects.

E. Cooking with Oxygen -- Zimpro

1. High temperature to destroy organic solids (450° C)
2. Low temperature to get good filterability (250° C)
3. Produces "soup" that is difficult to treat.
4. Disinfects.
5. Power recovery not economical.

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FWPCA-SUPPORTED RESEARCH IN THE OHIO BASIN REGION

Robert L. Feder

I. INTRODUCTION

A. Research and development in the water pollution control field can be and is a wide ranging field of endeavor. Involved are not only such fields as the physical, chemical and biological sciences, but also economics, sociology and law. Each of these is important in its own right, and each is involved in one way or another in the research activities of the Federal Water Pollution Control Administration.

B. The Federal Water Pollution Control Administration is involved in a wide spectrum of research and development activities. These activities are carried out through internal research efforts at FWPCA laboratories or through financial support to others doing needed research. Financial support is provided through a variety of grant and contract programs.

C. The internal research activities of the Federal Water Pollution Control Administration are carried out at several laboratories in different regions of the nation. Each laboratory has one or more specific national research assignments. The oldest and largest FWPCA laboratory, the Robert A. Taft Center, is located in the Ohio Basin at Cincinnati. The assignments of this laboratory, in addition to advanced waste treatment research, include analytical quality control research and mine drainage activities. The efforts and accomplishments of this laboratory have been presented in some detail during this symposium and need no further amplification.

D. Extra-mural research and development activities, i.e., those carried out by grant and contract support, are also a part of national programs. Grants and contracts are awarded on the basis of project merit, regardless of geographical location. A brief review of some of these activities now underway in the Ohio River Basin will serve to give an insight into the programs.

II. FWPCA GRANT AND CONTRACT PROGRAMS

A. Perhaps the easiest way to interpret the research and development activities receiving federal support is to understand the programs themselves. Of most interest are the five grant programs. Although this sounds like a large number of programs, they are actually interrelated and similar. All are directed toward finding solutions to the problems of water pollution control.

B. The first two grant programs are awarded to public or private agencies, institutions or individuals at not more than 95% of the project cost. The two grant types and the activities to which they are directed are:

1. Research Grants - Awarded to assist in supporting basic and applied research related to the causes, control and prevention of water pollution.

2. Demonstration Grants - Awarded to assist in investigations and studies developing and demonstrating the feasibility of new methods related to the causes, control and prevention of water pollution.

C. The remaining three grant programs are directed toward developing and demonstrating solutions to specific pollution problems. These problems are:

1. Storm and Combined Sewer Overflows

2. Advanced Waste Treatment and Joint Treatment of Municipal and Industrial Wastes

3. Control of Pollution by Industry

D. In addition to grants, research and development work may be supported by contracts. The terms grant and contract are sometimes interchanged, but there are significant differences. Some of these are:

1. Grants

   a. Federal financial support is always less than 100%.

   b. Grantee has definite interest in conduct of the project because of financial commitment.

   c. For some grant projects, permanent facilities may result.

   d. No fee is involved.

2. Contracts

   a. Financial support is usually 100%.

   b. Work supported by the contract is specific. Very close supervision of the project conduct is normal.

   c. Permanent facilities do not result.

   d. Contractor usually receives some specified compensation over and above actual project costs.

E. Although there are basic differences between grants and contracts, work done under each is directed toward the goal of uncovering solutions. This common feature is far more important than the mechanical differences. The sections which follow briefly describe selected FWPCA-supported grant projects currently underway in the Ohio Basin Region.

III. RESEARCH GRANT PROJECTS

A. Research grants are awarded at a level of 95% or less of the total project costs to public or private agencies, institutions or individuals for projects directed toward the discovery and development of new information and technology related to:

1. Identification of pollutants.
2. Fate and persistence of pollutants.
3. Effects of pollutants on water uses.
4. Treatment processes.
5. Non-treatment methods of pollution control
6. Ultimate disposal of pollutants.

B. Specific examples of research grant projects in the Ohio Basin Region are:

1. "Mechanisms of Sludge Thickening" - University of Illinois, Urbana, Illinois.
    a. Principal Investigator - Dr. Richard I. Dick (Ph.D.)
    b. Description - Under this grant, the fundamental mechanisms which control the settling behavior of concentrated sludges are being evaluated. Theories of flow through porous media have been used to analyze observed settling behavior of flocculent sludges. The technique has permitted study of the changes in floc diameter and water content which occur as thickening takes place. In other studies, a coaxial cylinder viscometer has been used to study the rheology of biological sludges and to observe the changes in the physical characteristics of biological sludges effected by changes in environmental conditions such as organic loading intensity. The thickening characteristics of biological sludges in full scale settling tanks is being studied to permit comparison with observed laboratory results and to permit development of rational criteria for design of sludge thickeners.
2. "The Effects of Inorganic Sediment on Stream Ecosystems" - De Pauw University, Greencastle, Indiana
    a. Principal Investigator - Dr. James R. Gammon (Ph.D.)

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b. Description - The basic purpose of this research project is to quantify the effect of inorganic pollution in the form of stonedust from quarrying and milling operations on certain biotic components of the stream. The study is being carried out under actual field conditions in a stream in central Indiana. The apparent effects of the dust on aquatic life at various points and under various conditions in the stream is being studied.

3. "Study of the Sulfide-to-Sulfate Reaction Mechanism" - Ohio State University Research Foundation, Columbus, Ohio

   a. Principal Investigator - Dr. Edwin E. Smith (Ph.D.)

   b. Description - This project is designed to determine the important physical and chemical parameters related to the kinetics of the sulfide-to-sulfate reaction. The data observed will be interpreted in light of suggested mechanisms to explain the observed kinetics.

4. "A Pilot-Scale Study of Acid Mine Drainage" - Ohio State University Research Foundation, Columbus, Ohio.

   a. Project Site - Vinton County, Ohio

   b. Description - This contract project is complimentary to the previously listed project in that basic research is to be tied into field applications. The project is designed to establish a systems research approach to the investigation of acid mine drainage. The study will attempt to define the controlling factors and to assess the significance of acidic conditions in abandoned or currently inactive mines, and in areas of future mining. Attempts will be made to assess the characteristics of acid formation, to establish systems to monitor adequately the variables selected, and to attack the problem with suitable abatement measures.

IV. DEMONSTRATION GRANTS

A. Demonstration Grants are awarded to public or private agencies, institutions and individuals for investigations and studies of an applied nature and to develop and demonstrate the feasibility of new methods related to the causes, control and prevention of water pollution. Grants may cover up to 95% of the total project costs.

B. Examples of demonstration grant projects in the Ohio Basin Region are:

   1. "Automated Forecast Procedures for River Quality Management" - Ohio River Valley Water Sanitation Commission

a. Description - Thirteen electronic water quality monitors will be operated in the 168 miles of the Markland and McAlpine pools of the Ohio River for the hourly transmission of data on water quality characteristics to a central receiving and logging station. The objective of the project is to demonstrate the potential for integrating data from automatic remote water quality sensors, manually operated sampling stations, waste load reports, river flow forecasts, and meteorological information with a digital computer in order to provide continuous forecasts of river quality changes for use in water quality planning, management, and enforcement.

b. Total estimated project cost - $482,050 (Three Years)
$210,950 (First Year)

Federal Grant (First Year) - $150,950

2. "Treatment of Total Wastes from a Sole Leather Tannery"
University of Cincinnati, Cincinnati, Ohio

a. Principal Investigator - Dr. J. David Eye (Sc.D)

b. Description - The major objective of this demonstration project, located in Marlinton, West Virginia, is the treatment in a stratified anerobic-aerobic lagoon system of the total effluents from a sole leather tannery. A second objective will be to gather operational and performance data on all components of the waste management system.

Clarified and neutralized beamhouse wastes will be mixed with the spent vegetable tan liquors in a lagoon. A floating aerator will be used to continuously circulate and aerate the upper third of the wastes in the lagoon. The effluent from the primary lagoon will flow through an additional anaerobic-aerobic unit. Clarification of the final effluent may be required to remove the suspended biological solids. The wastes after leaving the third lagoon will either be discharged directly to the stream or blended with the domestic sewage for additional treatment.

V. STORM AND COMBINED SEWER PROJECTS

A. Research and development grants and contracts are awarded to assist projects which will develop and/or will demonstrate a new or improved method of controlling the discharge into any waters of untreated or inadequately treated sewage or other wastes from sewers which carry storm water and sewage or other wastes. Grants are awarded for up to 75% of the estimated reasonable project cost to states and interstate agencies, municipalities and intermunicipal agencies. Contracts are awarded to public and private agencies, institutions and individuals for up to 100% of the project cost, primarily for projects of a developmental nature.

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B. Storm and combined sewer grant projects underway in the Ohio Basin include:

1. "Modification of Whittier Street Storm Standby Tanks" - City of Columbus, Ohio

   a. Description - The City of Columbus has in existence three adjacent combined sewer overflow tanks having a capacity of 1.3 mg each. These tanks have recently been renovated by the installation of automatic controls for the tank sluice gates, new travelling bridge-type sludge collectors and new pumps. One objective of the automation is to keep sludge levels low by continuously removing it from the tanks and thereby preventing anaerobic decomposition and its resultant odors. Another objective is to control flows at the treatment plant by proper use of the automatically operated sluice gates.

   The project consists of an evaluation of the pollution reduction effectiveness of the modernized tanks. Evaluation will include studies of the efficiency of the tanks as treatment units as well as studies of the effect of the system on the Scioto River.

   b. Total estimated project cost (including renovation)-$1,231,519

   Federal Grant -$ 300,000

2. "The Determination of Ground Water Infiltration and the Effects of Internal Chemical Sealing of Sanitary Sewers" - Montgomery County, Ohio.

   a. Description - A demonstration program is to be carried out which will attempt to identify the cause and degree of infiltration of surface and ground water into a selected sanitary sewer system. Remedial action will then be taken utilizing internal sewer sealing techniques. Appropriate, new techniques will be tried and evaluated. Effectiveness and cost data will be analyzed to establish the most effective techniques and materials.

   b. Total estimated project cost - $137,000

   Federal Grant - $ 96,570

VI. ADVANCED WASTE TREATMENT AND JOINT TREATMENT PROJECTS

A. Research and development grants and contracts are awarded to assist projects which will develop and/or will demonstrate advanced waste treatment or water purification methods, or new or improved methods of joint treatment systems for municipal and industrial wastes. Grants are awarded for up to 75% of the estimated reasonable project cost to states and interstate agencies, municipalities and intermunicipal agencies. Contracts are awarded to public and private agencies, institutions, and individuals for up to 100% of the project cost.

B. Projects in the Ohio Basin Region include:

1. "Conversion of Existing Anaerobic Digesters to Aerobic Digesters - Full Plant Scale" - City of Hamilton, Ohio

a. Description - The City of Hamilton, located on the Great Miami River in Southwestern Ohio, is equipped with a split-treatment activated sludge sewage plant (12 mgd primary treatment, 6 mgd secondary treatment). Separate sludge digestion and vacuum filtration are included. The wastewater received is somewhat atypical because of a one million gallon daily contribution by a local industry. This waste contributes a high percentage of the raw sewage solids and appears to be partly responsible for the continuous difficulty with anaerobic digestion encountered at the plant.

The research project involves the conversion of two existing floating cover digesters (80 ft. diameter, 15 ft. sidewall) to aerobic units. After conversion, the covers will rest on the ledge and will be properly vented. The installation will include three 3000 cfm blowers equipped with ammeter type flow indicators. Diffusion will be a 96" diameter eductor tube in each digester.

One converted digester will be operated on a carefully controlled program of varied sludge volumes, aeration rates and temperatures using a mixture of raw primary and waste activated sludge. The other unit will take the excess sludge. Vacuum filtration of the aerobically digested sludge will also be examined.

b. Total estimated project cost - $342,406

Federal Grant - $241,804

2. "Development of a Fluidized-Bed Technique for the Regeneration of Powdered Activated Carbon" - Battelle Memorial Institute, Columbus, Ohio.

a. Description - Dissolved organics can be removed from wastewater by utilizing a powdered carbon adsorption process. A method for re-establishing the original adsorptive capacity to the spent powdered carbon must be developed to make the process economically attractive. Accordingly, the subject contract was awarded to evaluate a method to accomplish regeneration.

A unit will be constructed and evaluated to apply fluidization methods for regeneration of spent powdered carbon. A fluidized bed of coarse, inert particles will be used as a constant temperature zone. The spent, dried, powdered carbon would be fed into the bottom of the coarse, inert bed and carried through the inert bed by the action of the fluidizing gas. This method of fluidized-bed operation should offer control of retention time of the powdered carbon and good heat-transfer characteristics. The finely divided carbon would be recovered with cyclone collectors on some other collection device.

b. Contract Amount - $55,900

VII. INDUSTRIAL WASTE POLLUTION CONTROL PROJECTS

A. Research and development grants are awarded to public and private agencies, institutions and to individuals to support research and demonstration projects for the prevention of pollution of waters by industry, including, but not limited to, treatment of industrial waste. These grants are awarded for as much as 70% of the estimated reasonable project cost. The maximum award for any one project is $1 million. A major criteria for grants awarded under this program is that the project must serve a useful purpose in the development or demonstration of a new or improved method of treating industrial waste or otherwise preventing pollution of waters by industry, which method shall have industry-wide application.

B. Industrial waste research and development grant projects in the Ohio Basin Region include:

1. "Treatment of Waste Water - Waste Oil Mixtures" - Armco Steel Corporation, Ashland, Kentucky.

a. Description - Development of modern cold-rolling mills in the steel industry has resulted in the generation of vast quantities of wastewater containing emulsified oils. Methods of treating such wastes prior to disposal are needed to prevent pollution of the nation's streams. This project provides for design, operation, studies and reports on a full scale demonstration facility built for the treatment of the oil-water emulsion wastes from a five-stand cold-rolling mill. A five chemical treatment method of coagulation and flocculation, followed by dissolved air flotation comprise the system. The oil-laden sludge which will result will be transferred to a heated mixer-clarifier for a few days retention prior to final incineration.

This project will not only demonstrate the process on a full scale, but will also assist in developing parameters of chemical dosage, flotation cell operation, and process control. A determination of realistic operating costs will be included.

b. Total estimated project cost - $1,541,720

Federal Grant - $ 209,000

2. "Treatment of Acid Rinse Waters" - Armco Steel Corporation, Middletown, Ohio.

   a. Description - One of the more difficult waste disposal problems facing the steel industry is treatment of large volumes of rinse waters resulting from the rinsing operations of continuous hydrochloric acid pickling. Methods are needed which are simple, efficient, economical and easily controlled.

   This project will involve treatment of about 1,500 gallons per minute of acid rinse and fume scrubber waters. This waste will be treated by the addition of powdered limestone to neutralize the free acid and to react with the iron chlorides. The latter will, upon aeration in the presence of pre-formed sludge, form ferric hydroxide floc and soluble calcium chloride. A unique feature of the process is complete oxidation resulting from the use of limestone. The ferric hydroxide gel and the insoluble limestone solids will be flocculated by oscillating paddles to cause their agglomeration into readily settleable masses which will subsequently be separated in a clarifier. Coagulant aids will be used to improve efficiency. Effluent from the clarifier will flow through a final lagoon where variations in quality are expected to be equalized. Sludge from the process will be dewatered on vacuum filters.

   Among the parameters to be demonstrated by the project are types, dosage rates, and points of addition for limestone and coagulant aids, different sludge recirculation rates, and the effect of different rates for mixing, aeration, flocculation, clarification and filtration.

   b. Total estimated project cost - $1,784,800

   Federal Grant - $ 547,500

3. "Anerobic Treatment of Synthetic Organic Wastes" - Union Carbide Corporation, South Charleston, West Virginia.

   a. Description - This project includes laboratory and pilot-scale work to determine the economic and technical feasibility of treating in anaerobic processes wastewater from a large synthetic organic chemicals plant. The effect of key variables such as solids containment, organic loading, mixing, temperature, pH and retention time will be determined.

Studies will be conducted at three scales: bench-scale, semi-pilot and pilot (15,000 gallon). A number of systems will be tested on the bench-scale and pilot-scale studies. Data from the most promising anaerobic systems of the bench and semi-pilot studies will be used to design and construct the pilot unit. This pilot unit will include treatment of the anaerobic effluent in a small aerobic system.

b. Total estimated project cost - $314,859
Federal Grant - $220,400

4. "Evaluation of Role of High Rate Trickling Filters and Aeration Devices Separately and in Combination for the Advanced Biological Treatment of Integrated Kraft Pulp and Paper Mill Effluents" - Mead Corporation, Chillicothe, Ohio

   a. Description - The activated sludge process is both a difficult-to-operate and expensive treatment process for the pulp and paper industry. This project is an attempt to find alternatives. The project involves the continuous operation of a pilot treatment plant containing plastic-media trickling filters, a brush-aerated oxidation ditch, conventional aerated lagoon, and two clarifiers. These units can be operated in parallel or in various combinations.

      The specific goals of the project are to determine the effect of influent quality on biological treatment, evaluate the potential of plastic-media trickling filters alone and in combination with the brush-aerated oxidation ditch and aerated lagoon, and to achieve higher than conventional BOD removals from Kraft mill wastes.

   b. Total estimated project cost - $401,476
      Federal Grant - $281,033

5. "Optimization and Development of Improved Chemical Techniques for the Treatment of Coal Mine Drainage" - Commonwealth of Pennsylvania

   a. Subcontractor - Bituminous Coal Research, Incorporated, Monroeville, Pennsylvania

   b. Description - This project involves laboratory studies to develop an improved process for the control and prevention of water pollution by drainage from coal mines. Included are a literature search, bench-scale studies and process design, evaluation and application. The basic process is the use of limestone for neutralization. Various catalysts for increasing the iron oxidation rate will also be evaluated.

c. Total estimated project cost - $150,000

Federal Grant - $105,000

6. "Evaluation of Pollution Abatement Procedures in the Moraine State Park, Butler County, Pennsylvania" - Commonwealth of Pennsylvania

a. Subcontractor - Gwin Engineers

b. Description - The project seeks to ascertain the effectiveness of various remedial procedures which have been applied to a large western Pennsylvania state park so that judgement may be made relative to widespread application of the procedures to specific pollution abatement projects. Water quality and quantity measurements will be made at sampling points throughout the Muddy Creek Watershed.

c. Total estimated project cost - $21,600

Federal Grant - $15,120

VIII. TOTAL RESEARCH & DEVELOPMENT GRANT ACTIVITY IN THE OHIO BASIN

A. The Federal Water Pollution Control Administration, through a variety of grant and contract programs, is actively providing financial support to a wide range of research, development and demonstration projects in the pollution control field. These projects are generally directed toward applied solutions. Grants are awarded on the basis of project merit, without regard to physical location.

B. On April 1, 1969, there were active in the Ohio River Basin 50 grant and contract projects representing a total federal investment of more than $5,454,000.

C. Information on the grant programs, whether it be related to active projects or procedures for applying, is available from the Regional Research and Development Office, Ohio Basin Region, FWPCA. Comments and suggestions on research that is needed will also be gratefully received.